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SULFUR DIOXIDE PHOTOOXIDATION RATES AND AEROSOL FORMATION MECHANISMS A SMOG CHAMBER STUDY

CALSPAN CORPORATION, BUFFALO, NEW YORK

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A Smog Chamber Study

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Section 1

INTRODUCTION

One of the principal concerns facing atmospheric scientists today lies in our lack of basic knowledge of aerosol behavior in the polluted atmosphere. Work has progressed in understanding aerosol formation mechanisms, but few dependable models of aerosol development have emerged. Indeed, even in the relatively simple SO_2 system, only the mechanics of aerosol behavior are reasonably well understood. The actual mechanisms responsible for aerosol development, however, must still be determined.

The ubiquitous presence of SO_2 in the urban atmosphere makes it one of the key pollutants requiring our research attention. While its presence is known to be responsible for the production of significant sulfate-containing aerosol, the SO_2 photooxidation rate in the presence of various impurities is not well established and needs to be known. Smog chamber data suggest an SO_2 photooxidation rate in clean filtered air of a few tenths of a percent per hour or less. In the presence of reactive hydrocarbons and oxides of nitrogen, higher rates of up to a few percent per hour are frequently observed.

It has been the objective of this investigation to obtain chamber irradiation data on various systems ranging from HC + NO_x + SO_2 to the clean air + SO_2 mix. Emphasis has been placed on examining the rates of SO_2 photooxidation in these systems and in chemically characterizing the aerosols which are formed. Midway through this year's program aerosol collections and routine sulfate analysis were initiated. Late in the period, nitrate and ammonia analysis procedures were also performed. Discussions are presented of several smog chamber systems that were tested. These include SO_2 + clean air (Section 3), propylene + NO_x + SO_2 (Section 4), an inorganic system of CO + NO_x + SO_2 (Section 5), and rural air + SO_2 (Section 6). The rationale for choosing these systems is also provided within the text. A summary and conclusions of this year's findings is given in Section 7.

Section 2

EXPERIMENTAL FACILITIES

The smog chamber used at Calspan (Kocmond et al., 1973) consists of a cylindrical chamber 30 feet (9.14 meters) in diameter and 30 feet (9.14 meters) high enclosing a volume of 20,800 ft^3 (590 m^3). The 1.25 cm thick chamber walls are coated with a specially-formulated fluoroepoxy-type urethane which has surface energy and reactivity properties comparable to those of FEP Teflon. Illumination within the chamber is provided by 28.6 kw of fluorescent blacklight and sun lamps installed inside 24 lighting modules and arranged in eight vertical channels attached to the wall of the chamber. Each lighting module contains two 40-watt sun lamps, eight 85-watt high output black lamps, and two 215-watt specially-produced black lamps. The lighting modules are covered with 0.5 cm Pyrex glass and are sealed from the chamber working volume. Measured light intensity using the $k_d[NO_2]$ method reported by Stedman & Niki is k_d~0.35 min^{-1}.

Chamber air is purified through a recirculation system consisting of a series of absolute and activated charcoal filters. Nearly all gaseous contaminants and particulate matter can be removed from the chamber air in about four to five hours of filtration. Filtered air generally contains no measurable particles, less than 0.1 ppm NO_x, 0.2 ppmC non-methane HC, and no measurable SO_2 or ozone.

New this year is a chamber washdown system, a humidifier, and a dehumidification system. The recirculating washdown system consists of a stainless steel spray head which rotates on two axis and can wet all of the chamber surfaces with distilled water or cleaning solution. Generally, the procedure is to first wash the chamber surfaces with a 5% solution of a laboratory glass cleaning agent followed by two or three rinsings with tap water and two final rinsings with distilled water. Drying is accomplished by fresh air flushing followed by air filtration. Chamber humidity can be

increased by spraying distilled water into the chamber from a remotely-operated spray nozzle near the chamber top. Nuclei which are introduced by the evaporating spray droplets are removed by absolute particle filters during the air filtration cycle. Chamber dehumidification when needed is accomplished by passing the chamber air over refrigeration coils to remove excess water. The system was designed and fabricated at Calspan and is capable of controlling humidity down to about 20% RH.

Instrumentation used to monitor aerosol behavior and reactant concentrations within the chamber includes a Bendix Model 8002 chemiluminescent ozone analyzer, Model 8101-B nitrogen oxides analyzer, Model 8300 total sulfur analyzer, and the Model 8201 reactive hydrocarbon analyzer; a Hewlett-Packard 5750 gas chromatograph; a Thermo Systems Model 3030 Electrical Aerosol Analyzer (EAA); an MRI Integrating Nephelometer; a Gardner Associates' small particle detector; and a GE condensation nucleus counter. A Meloy flame photometric total sulfur analyzer on loan from the EPA was also used for most of the experiments. More complete descriptions of the chamber and analytical instrumentation facilities are given in an earlier Calspan report (Kocmond et al., 1973).

Section 3

THE SO_2-CLEAN AIR SYSTEM

Major emphasis on the current phase of this program has been placed on determining the SO_2 photooxidation rate (R_{SO_2}) in clean as well as contaminated atmospheres. Clean air + SO_2 irradiations are routinely performed to establish chamber reactivity and to gauge the effect of previous experiments on H_2SO_4 aerosol formation. In the past, SO_2 photooxidation rates, as determined from aerosol analyzer data, have been in the range of a few tenths of a percent per hour in clean filtered air. The effect of certain pollutants, especially reactive hydrocarbons, is to enhance R_{SO_2} appreciably.

The production of aerosol from SO_2 photooxidation is generally attributable to chemical conversion of SO_2 to SO_3 followed by rapid reactions with normally-occurring atmospheric constituents, such as H_2O and NH_3, to form condensable products. Under clean atmospheric conditions, therefore, sulfuric acid formation from SO_2 may be expected to proceed via the following sequence of reactions (A.W. Castleman, Jr. et al., 1975):

(1) Oxidation of SO_2 to SO_3
(2) Reaction of SO_3 with water to yield H_2SO_4
(3) Clustering of H_2SO_4 and water molecules to form pre-nucleation embryos.

An understanding of the detailed mechanism of SO_2 conversion to SO_3 in the ambient atmosphere is still lacking. Homogeneous photolysis of SO_2 via solar radiation in the 2400-3400 Å range would give an oxidation rate far less than that normally observed even in the unpolluted atmosphere (J.P. Friend et al., 1973). The actual rate of SO_2 photooxidation must therefore occur as a synergistic effect due to the presence of other trace reactive contaminants in the atmosphere. A number of different reaction schemes of SO_2 oxidation by free radical and active oxygen intermediates have been suggested to account for the observed ambient monitoring data. A summation of

the current understanding of the chemical kinetic schemes providing a reasonable account of atmospheric SO_2 photooxidation is given by Calvert and McQuigg (1975).

It is generally agreed that, even in the relatively unpolluted atmosphere, OH radicals may be generated by naturally-occurring photochemical processes giving rise to concentrations of the order of 10^6 cm^{-3}. The reaction of OH radicals with SO_2 is considered to be a key process contributing to atmospheric SO_2 oxidation. Ozone and HO_2 radicals are present at higher concentrations but contribute to SO_2 oxidation to a lesser extent because of the considerably slower specific reaction rates. The specific rate constants for SO_2 reactions with alkyl oxyl and alkyl peroxyl radicals are not available as experimental estimates. These reactive intermediates would, however, be relatively unimportant in the unpolluted atmosphere. In the hydrocarbon and NO_x polluted atmosphere, the alkyl oxyl and alkyl peroxyl radicals may contribute to the overall SO_2 oxidation process to a more significant extent. Another important factor in the polluted atmosphere lies in the possibility of a synergistic effect of ozone and olefins on SO_2 oxidation. Such a possibility has been suggested by Cox and Penkett (1971, 1972). According to Calvert and McQuigg (1975), a diradical $\cdot OCH_2O\cdot$ species may be generated from ozone-olefin reactions, and it may serve as an effective reaction intermediate for SO_2 oxidation.

Reviews of the general mechanisms of the physical aspects of aerosol formation, growth, and decay in the SO_2-clean air system can be found in Clark (1972) and Kocmond et al. (1975). Briefly, however, three main mechanisms govern aerosol behavior in these systems: nucleation, condensation, and coagulation. Initially, after the lights are turned on, homogeneous nucleation of the newly-formed condensable product species occurs to form new particles in the supersaturated vapor mixture. Once formed, the particles continue to grow through condensation of the vapors and new product molecules onto their surfaces. The rate of condensation depends primarily on the degree of supersaturation, the diffusion coefficient, and the size of the particle itself. Although condensation does not affect the particle concentration, it does

result in increased particle surface and volume concentrations. The third process, coagulation, refers to the collision and striking of particles with one another. Here, the rate of coagulation is proportional to the square of the particle number. Coagulation leads to a decrease in particle number and surface concentration but does not affect the volume concentration.

For the SO_2 + clean air system, we have stated that the rate of aerosol volume production approaches a constant value and that a plot of volume against time yields a straight line (Clark, 1972; Kocmond et al., 1975) over a reasonably long period of time. The reasoning was that the rate of oxidation of SO_2 to SO_3 was equal to the rate of removal of SO_3 to form sulfuric acid droplets. The rate of production of H_2SO_4 aerosol, corrected for molecular weight change and water concentration, would therefore equal the rate of photooxidation of SO_2 which is constant during the linear growth phase of the experiments. Under these conditions, the slope of the straight line volume growth curve can be related directly to the rate of photooxidation of SO_2 according to:

$$-\frac{d[SO_2]}{dt} = \frac{dv}{dt} \times \rho \times \underline{P} \times \frac{MW_1}{MW_2} \qquad (1)$$

where ρ is the density of the H_2SO_4 droplet, $\underline{P}$ is the weight fraction of H_2SO_4 in the drop, MW_1 is the molecular weight of SO_2, and MW_2 is the molecular weight of H_2SO_4.

The above equation is true if one assumes that (1) all of the SO_3 formed combines with water to form H_2SO_4 droplets; (2) the sulfuric acid droplets are in equilibrium with the water vapor in the gas phase; and (3) the droplets are represented by a pure H_2SO_4 solution. For a clean, contamination-free system, these assumptions appear valid; however, in the presence of even small amounts of particulates, reactive hydrocarbons or nitrogen oxide species, large deviations from linearity can be expected with attendant accelerated aerosol growth. In addition to homogeneous gas-phase reactions involving the reactive intermediates generated from trace contaminants,

heterogeneous paths may also contribute to accelerated SO_2 oxidation and aerosol growth. The Calspan chamber with its relatively small surface to volume ratio is especially suited to studies of heterogeneous reaction effects, as well as the mechanics of aerosol growth and decay in the atmosphere. Experiments have therefore been directed toward the aerosol characterization and formation rate data relevant to the interpretation of atmospheric SO_2 photooxidation. The photooxidation rates reported here are based mainly on interpolations of the EAA aerosol data. The initial and max rates are calculated respectively from the data over an initial low growth period and a relatively short interval of active aerosol development. The photooxidation rates so computed must be regarded as excessively high whenever non-sulfate aerosols are also being produced.

3.1 Data Summary -- SO_2-Containing Systems

Careful examination of aerosol data from SO_2 + clean air experiments performed during the past year shows that in most cases there is a slight upward curvature in the volume growth during the late stage or about the second half of each experiment. A typical example of this behavior is shown in Figure 1. Here the volumetric growth curve rises slowly during the first 30 minutes or so and then increases rapidly thereafter. As noted in our previous discussion, this would suggest a role of trace contaminants in the air. According to Calvert and McQuigg (1975), contributions to SO_2 photooxidation by HO_2-SO_2 and OH-SO_2 reactions would reach maximum values after about 30 minutes in the slightly polluted air. As the SO_2 + clean air irradiation proceeds, reactive intermediates build up within the chamber (depending on the background levels of NO_x and contamination of chamber surfaces) and the photooxidation rate of SO_2 increases. Because of the upward curvature noted in most SO_2 + clean air experiments, three rates of SO_2 photooxidation are computed from the EAA data--one during the initial 30 to 45 minutes of the experiment, one during the maximum aerosol growth period of the experiment, and an average value computed for the full length of the experiment. Data for all SO_2 + clean air experiments performed during the past year are summarized in Table I. The table shows the experiment number, date, SO_2

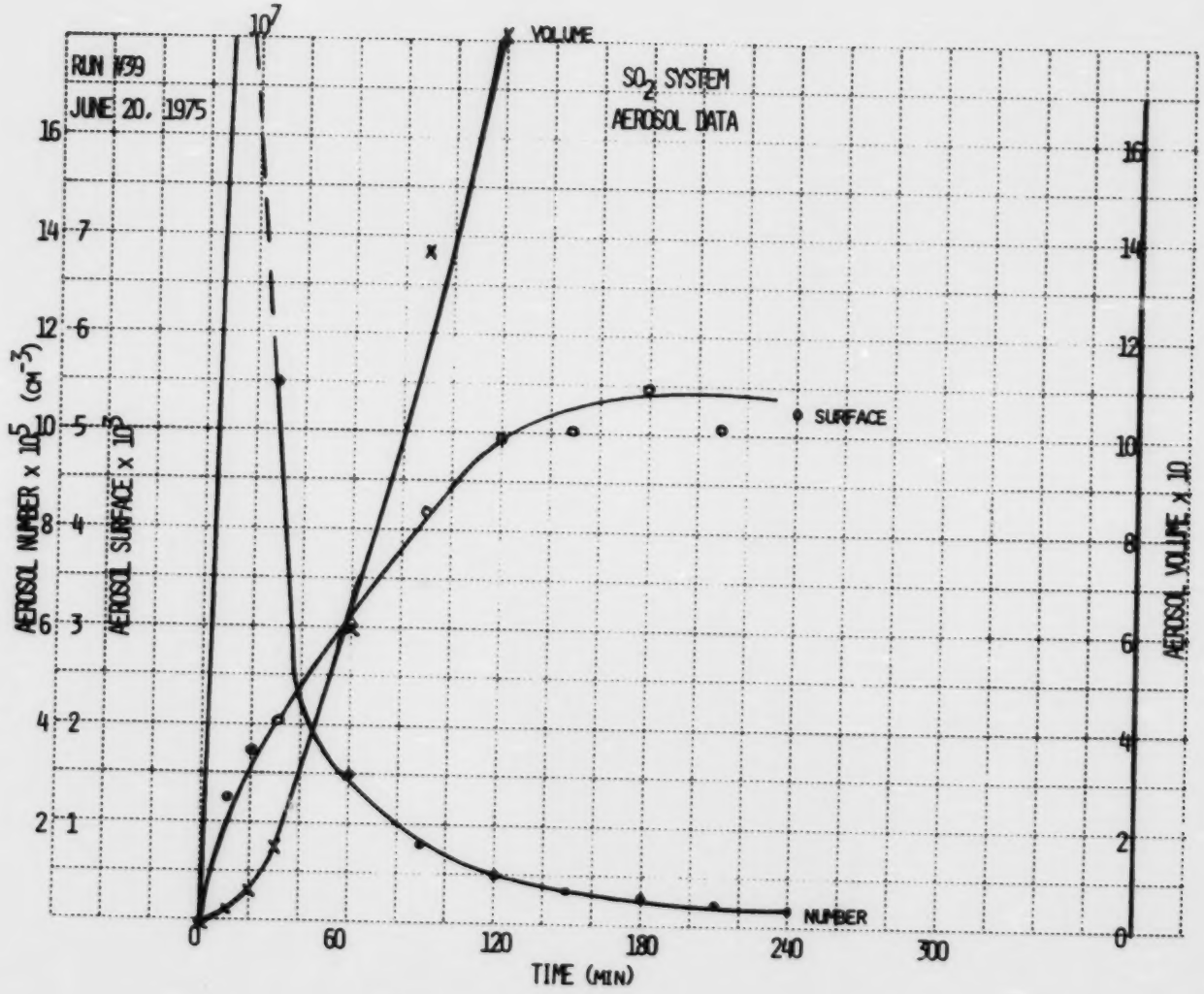

Figure 1 AEROSOL DEVELOPMENT IN THE SO_2 + CLEAN AIR SYSTEM

Table I.

SUMMARY OF "CLEAN AIR" SO_2 PHOTOOXIDATIONS

Run No.	Date	SO_2 Conc. ppm	RH %	Dark Rx	Irradiation Time min	$R_{SO_2(initial)}$ % hr^{-1}	$R_{SO_2(max)}$ % hr^{-1}	$R_{SO_2(ave)}$ % hr^{-1}
1	10/11/74	0.28	46	Yes	180	1.0	3.6	1.7
2	10/14/74	0.30	30	Yes	120	2.0	5.0	4.4
3,4	Clean Air Irradiations		-- CLEAN CHAMBER --					
5	10/16/74	0.25	48	Yes-Large	120	1.3	2.6	1.9
6	10/16/74	0.25	42	Yes	90	0.8	1.7	1.1
7	10/17/74	0.37	39	Yes	90	0.4	0.9	0.9
8	10/17/74	0.31	39	Small	120	0.2	0.2	0.2
9	10/18/74	0.36	41	No	60	0.5	0.7	0.6
10-17	Propylene + NO_x Irradiations							
18	2/11/75	0.42	30	No	210	0.2	3.0	1.4
19-23	Propylene + NO_x + SO_2 Irradiations							
		-- AUTO EXHAUST EXPERIMENTS--THEN CLEAN CHAMBER --						
23B	4/04/75	0.26	35	Yes-Large	75	11.1	9.7	8.5
24	4/04/75	0.38	38	Yes-Large	90	3.4	3.0	3.3
25	4/06/75	0.53	34	Yes-Large	90	2.8	2.8	2.5
26	4/07/75	0.50	45	Yes-Large	120	3.7	3.7	3.2
27-29	Inorganic Test Series							
30	4/12/75	0.96	22	Small	60	0.6	0.9	0.9
32	4/17/75	0.54	25	Small	90	0.5	1.2	1.0
33-36	Inorganic Test Series							
37	6/16/75	0.68	55	Small	60	1.4	4.6	3.0
38	6/20/75	1.00	63	Small	60	0.5	1.7	1.7
39	6/20/75	0.76	30	No	240	0.7	3.4	1.6
40	6/23/75	0.70	35	No	330	0.4	3.8	2.1
41	6/24/75	0.60	41	No	240	0.4	2.7	2.1
42-44	Rural Air Irradiations							
45	7/2/75	0.58	40	No	420	0.5	2.1	1.2
46-48	Rural Air Irradiations							
49	7/17/75	0.55	65	No	---	0.5	1.4	0.7
50	8/25/75	0.54	61	No	90	0.2	1.6	1.1
51-53	Filtered Rural Air + SO_2							
54	8/29/75	0.50	50	No	90	0.1	0.9	0.5

concentration at the beginning of the experiment, relative humidity, presence or absence of a dark reaction, irradiation time, and the computed SO_2 photooxidation rates as described above. Aerosol and chemistry data for these experiments are provided in Appendix A.

Observed variations in the specific SO_2 oxidation rate appear to be rather insensitive to limited changes in some of the common experimental variables, such as relative humidity, SO_2 concentration or chamber size. On the other hand, the history of chamber conditioning arising from preceding experiments does seem to have an influence on the results in that somewhat higher rates are usually observed after first completing experiments using auto exhaust or reactive hydrocarbons in the presence of NO_x. What appears to be a positive indicator of a reactive SO_2 system is the presence of a dark reaction after admitting SO_2 into the chamber. Some of these effects can be seen from the dark reaction data shown in Table I.

The first two experiments of the entire test series were conducted after having just completed several auto exhaust irradiations on another EPA program (Contract No. 68-02-0698). In both tests, there was a large dark reaction prior to irradiation as well as enhanced SO_2 photooxidation. After cleaning and rinsing the chamber with distilled water, two clean air irradiations were performed to test for background reactions. In both instances, no appreciable particle formation was observed.

Experiments 5-9 were repetitive SO_2 irradiations in clean air. Here, as in previous instances, a conditioning effect was noted in that each successive irradiation produced a slightly lower SO_2 photooxidation rate. The conditioning effect was also manifested in the form of a decreasing dark reaction after each successive SO_2 experiment. It is likely that the conditioning process results in the destruction or other losses of contaminants within the chamber, which would presumably result in a lessening of the SO_2 oxidation rate. Desorption of HONO (HONO $\xrightarrow[h\nu]{k}$ HO + NO) from chamber surfaces may, for example, occur to a lesser extent with each successive irradiation.

On the other hand, after performing several HC-NO_x experiments, renewed formation of HONO may result in substantial contamination of chamber surfaces requiring additional conditioning to achieve low R_{SO_2}. If the chamber surfaces are badly contaminated, a large number of SO_2 conditioning tests may be required before any appreciable reduction in R_{SO_2} is observed.

The second series of experiments seem to bear out this assessment. Experiments 10-17 and 19-23 were performed as part of the chamber intercomparison test series involving propylene + NO_x and propylene + NO_x + SO_2 irradiations. Following these experiments, a number of auto exhaust irradiations were performed. In spite of cleaning and rinsing the chamber surfaces after these tests, the next several SO_2 + clean air irradiations produced large dark reactions and much higher than usual SO_2 photooxidation rates. In fact, the rates observed in this particular test series (23B-26) were the highest ever observed at Calspan for SO_2 + clean air irradiations.

Following the above experiments, an inorganic test series was performed (experiments 27-29 and 33-36) in which various amounts of CO was introduced into the NO_x + SO_2 system. Different levels of carbon monoxide ranging from background concentrations of less than 10 ppb to 400 ppm were irradiated in the presence of SO_2 + NO_x in an effort to evaluate the possible effects of CO on R_{SO_2}. (The significance of these experiments is discussed in more detail in Section 5.) It is worth noting that for this series of tests, as well as the subsequent SO_2 + clean air experiments (experiments 30 and 32 and 37-41), R_{SO_2} (initial) was at significantly lower values. On the other hand, $R_{SO_2(ave)}$ still was relatively high suggesting that surface contamination or reactive intermediate production or both were not completely eliminated. Note also that the amount of dark reaction in the later tests was much lower indicating a less reactive system.

The final series of experiments involving rural air + SO_2 irradiations with and without natural nuclei was designed to test for accelerative effects of natural nuclei on the heterogeneous oxidation of SO_2. Interposed

between the rural air tests, SO_2 + clean air irradiations were performed. The experiments, numbers 45, 49, 50 and 54, show a distinct chamber conditioning effect in terms of reduced value of the initial, maximum, and average R_{SO_2}. Since only rural background levels of hydrocarbon and NO_x (less than 0.2 ppm non-methane HC and <0.02 NO_x) were used in this test series, no significant contamination of the chamber air or its surfaces occurred between the SO_2 + clean air irradiations. This is further evidenced by the fact that no appreciable dark reaction was observed after introducing SO_2 into the chamber for any of the last few experiments. The range of SO_2 photooxidation rates in experiments 45, 49, 50 and 54 may be taken as typical of the Calspan chamber after conditioning, i.e., from a few tenths of a percent per hour to slightly greater than 1% hr^{-1}.

3.2 Comparison of Sulfate Analysis by the Barium Perchlorate Method with EAA Data

Midway through this year's program, an effort was made to develop microanalytical capabilities for direct determination of sulfate content of the aerosol using the barium perchlorate titration method (Fielder and Morgan, 1960). Determinations of R_{SO_2} could then be made and compared with apparent photooxidation rates as computed from EAA data. For several of the experiments, analytical results were checked by independent analysis of filter samples at Battelle. Ammonium analysis was also provided by Battelle for several of the runs and by Calspan for the last few experiments of the entire test series. In this section, results of some of the experiments are presented and compared with EAA data where possible.

- Analysis Procedure

In the initial series of sulfate aerosol analyses, samples were collected with a two-inch diameter Gelman inline filter holder, with the total air volume for each sample about 1 m^3. Prewashed Tissuquartz filters were used to minimize the possibility of on-filter oxidation of SO_2. The sulfate content for each aliquot filter sample was only slightly greater than the detectability

limity of the barium perchlorate titration technique. Consequently, the analytical results were found to be unsatisfactory, both with respect to comparison with EAA data and from comparison of Calspan and Battelle results.

For the later experiments, a 142 mm diameter Gelman inline filter holder was used to acquire aerosol samples. This permitted the sampling of air volumes in the range of 7 m^3 to 15 m^3 within convenient sampling periods. For experiments 39 on, one-half of each filter sample was delivered to Battelle for analysis. The remaining half of each sample was analyzed at Calspan according to the following method.

Each filter sample was digested over low heat for about an hour in 20 ml of distilled water. The sample was filtered, adjusted to alkaline pH with two drops of 0.02 N NaOH and then reduced to 10 ml by evaporation over low heat. Forty ml isopropanol was added to each sample to make up a 4:1 isopropanol-water solution of 50 ml total volume. The sulfate content in each sample was determined by titration with 0.0048 N barium perchlorate to the thorin indicator end point. Ammonium analysis was performed by digestion of the filter sample in distilled water with the addition of two drops of 0.05 N H_2SO_4. The resulting solution was filtered and concentrated to 10 ml by evaporation over slow heat. Analysis of the solution was then performed with a gas-sensing ammonium ion specific electrode.

Analysis results for a number of experiments are summarized in Table II. The table shows the experimental conditions, initial SO_2 concentration, sulfate content of the collected aerosol, computed SO_2 oxidation rate, initial and maximum SO_2 oxidation rate as determined from EAA data, NH_4^+ content and stoichiometric NH_4^+ to sulfate ratio.

It may be noted from the data in Table II that the results tend to agree best with the "initial" SO_2 photooxidation rates as determined from the EAA data. In this respect, the data are in good agreement for the SO_2 + clean air and SO_2 + NO_x + CO systems. The apparent lack of agreement between the

Table II. AEROSOL SAMPLE SULFATE AND AMMONIUM CONTENT

Run No. & Conditions	Initial SO_2 Conc., ppm	Sulfate Content $\mu g/m^3$	SO_2 Ox. Rate, %/hr	R_{SO_2}(initial) EAA Data %/hr	R_{SO_2}(max) EAA Data %/hr	R_{SO_2}(ave) EAA Data %/hr	NH_4^+ Content $\mu g/m^3$	Stoichiometric NH_4^+ - Sulfate Ratio
31 SO_2 + NO_x + 100 ppmCO	0.60	--	---	0.3	0.9	0.6	--	---
33 SO_2 + NO_x + 100 ppmCO	0.56	12.2	0.2	0.4	1.0	0.6	--	---
34 SO_2 + NO_x + 400 ppmCO	0.46	27.8	0.5	0.5	1.1	0.8	--	---
36 SO_2 + NO_x + 400 ppmCO	0.45	13.0	0.2	0.3	1.2	0.8	--	---
39 SO_2 + clean air	0.76	44.0	0.5	0.7	3.4	1.6	--	---
40 SO_2 + clean air	0.70	46.9	0.5	0.4	3.8	2.1	--	---
41 SO_2 + clean air	0.60	46.4	0.6	0.4	2.7	2.1	--	---
42 Rural air	<0.01	.53	---	---	---		--	---
43 Rural air	<0.01	.67	---	---	---		--	---
44 Rural air	<0.01	4.9	0	0	0		8.1	4.4
45 SO_2 + clean air	0.58	39.3	0.4	0.5	2.1	1.2	13.9	0.9
46 SO_2 + rural air	0.52	35.2	0.5	2.0	2.3 ↓	0.8	17.2	1.3
47 SO_2 + rural air	0.48	25.2	0.4	1.2	1.6 ↓	0.8	17.7	1.9
48 SO_2 + rural air	0.52	23.6	0.3	1.0	1.4 ↓	1.1	15.7	1.8
51 SO_2 + filtered rural air	0.65	25.5	0.3	1.9 ↓	(Dark Rx)	1.1	16.5	1.7
52 SO_2 + filtered rural air	0.50	49.3	0.7	0.8	1.1	0.9	15.4	0.8
53 SO_2 + filtered rural air	0.54	22.8	0.3	1.1	1.2	0.7	13.1	1.5

sulfate analysis and $R_{SO_2(max)}$ and $R_{SO_2(ave)}$ for these systems suggests the presence of background contaminants which led to the formation of impurity aerosols other than sulfate. Under these conditions, the assumption that all aerosol formed is H_2SO_4 is obviously not valid. Indeed, the rather appreciable amounts of NH_4^+ in the samples lead to uncertainties in the interpretation of data obtained with the electrical aerosol analyzer during the later stages of the experiments. The EAA data can be interpreted to give the instantaneous SO_2 oxidation rates only when the aerosol composition, including the content of water of hydration, is well established. Aerosol loss, especially during the late stages of the experiment period, is difficult to avoid and therefore directly affects the results. It would appear from these data that initially nearly all of the aerosol formed is H_2SO_4 and that later into the experiment substantial contributions to aerosol development occur from impurities within the air or from contaminated chamber surfaces or both.

3.3 SO_2 in the Presence of Natural Nuclei

Evidence of initial catalytic effects on aerosol growth can be seen from the data summaries for experiments 46 through 53. In experiments 46, 47 and 48, unfiltered rural air containing natural nuclei was irradiated in the presence of SO_2. In almost every instance, the computed SO_2 oxidation rate based on sulfate determinations was much lower than that determined from the EAA data assuming acid aerosol. Apparently under these conditions, background impurities, as well as natural nuclei in the rural air, were sufficient to produce appreciable initial aerosol growth beyond that due to SO_2 photooxidation alone. In assuming that all of the aerosol formed was H_2SO_4, the EAA estimation of R_{SO_2} was obviously too high. After a relatively short time, the aerosol grew beyond the detection limits of the EAA and the apparent SO_2 oxidation rate decreases. Although we have followed the usual procedure of evaluating the EAA data in terms of $R_{SO_2(initial)}$, $R_{SO_2(max)}$, and $R_{SO_2(ave)}$, an obvious point of inflection in aerosol growth does not exist for the SO_2 + rural air irradiation rate data.

The data for experiments 51 through 53 show similar trends. Here, rural air was introduced into the chamber followed by absolute filtering to remove natural particles. No charcoal filtering of the air was attempted. After irradiating the sample for three hours, aerosol samples were collected for comparisons with EAA data. As before, R_{SO_2} based on the aerosol analyzer output was substantially higher than that determined from sulfate analysis. In these experiments, even after absolute filtering of the air, the presence of natural background levels of non-methane hydrocarbons, NO_x and O_3 were apparently sufficient to produce enhanced aerosol growth during the early stages of the experiments. The computation of a large SO_2 oxidation rate based solely on H_2SO_4 aerosol was therefore erroneously high, since aerosol sufficient to produce enhanced aerosol growth during the early stages of the experiments. The computation of a large SO_2 oxidation rate based solely on H_2SO_4 aerosol was therefore erroneously high, since aerosol composition was of mixed origin. The data indicate that the SO_2 photooxidation rate as computed from aerosol sulfate content falls within the range of 0.3 to 0.5 percent per hour regardless of whether the SO_2 is irradiated in natural rural air, with only the natural particulates removed or with cleaning through both absolute and charcoal filters. Initial aerosol production is enhanced somewhat over the SO_2 + clean air system, but after several hours of irradiation the SO_2 + clean air and SO_2 + rural air samples give comparable results in terms of aerosol development.

Comparisons of the Calspan and Battelle sulfate and, where available, NH_4^+ analyses are shown in Table III. The data as shown are in substantial agreement and give added confidence to the reliability of the analytical techniques. In order to minimize the effect of background contaminants, each of the quartz filters were individually washed with water distilled over permanganate and then recompressed and dried. This may have resulted in inhomogeneities in porosity, as well as aerosol particulate distribution over the filter. It is, therefore, not surprising to find up to 30% difference in analytical results for some of the samples.

Table III. COMPARISON OF CALSPAN AND BATTELLE ANALYTICAL RESULTS

Run No.	Origin	Calspan Analyses	Battelle Analyses	
		$SO_4^=$ µg/filter	$SO_4^=$ µg/filter	NH_4^+ µg/filter
39	Calspan	153	156	96
40	Calspan	246	350	144
41	Calspan	162	97	66
42	Calspan	2.8	< 10	< 2
43	Calspan	4.7	< 10	20
S-138	Battelle	1712	1230	220
S-140	Battelle	728	590	120

It is worth noting that the ammonium content for each of the filter samples analyzed fell within a narrow range of 96 to 146 μg per filter. Although inadvertent contamination of the filters must be considered, a more reasonable explanation is that the aerosol sulfate was generated from trace amounts of NH_3 in the chamber air. For the SO_2 photooxidation experiments, the NH_4^+ content of the aerosol samples ranged from 8.1 $\mu g/m^3$ to 19.1 $\mu g/m^3$. A residual NH_3 concentration in the chamber air of about 0.04 ppm would account for the aerosol ammonium measured. The fact that the observed $NH_4^+/SO_4^=$ stoichiometric ratio was greater at low sulfate concentrations tends to support the contention that the background chamber NH_3 content is the responsible factor for the observed aerosol NH_4^+ stoichiometry. At the rather low background NH_3 concentration conditions, NH_4^+ would be incorporated mainly by neutralization subsequent to an initial formation of sulfuric acid aerosol. In the absence of heterogeneous mechanisms, this low level NH_3 contamination is not expected to affect significantly the SO_2 photooxidation rates.

Section 4

PROPYLENE + NO_x AND PROPYLENE + NO_x + SO_2 EXPERIMENTS

This year, several propylene + NO_x and propylene + NO_x + SO_2 experiments were performed as part of a smog chamber intercomparison test series. The propylene + NO_x system has been subjected to data evaluation by extensive computer modeling of kinetic data in the past and offers a good opportunity for comparing chamber performance with model predictions. Summaries of the chemistry and aerosol data for these experiments and two corresponding Battelle experiments are given in Tables IV and V. In Table IV, the run number and date, reactant concentrations, and times to ozone and NO_2 maximum values are shown. Table V summarizes the maximum number concentration for each system, the initial volumetric production rate $[dv/dt]SO_2$, the computed initial SO_2 oxidation rate as determined from EAA data, and the maximum aerosol production rate [dv/dt]max, achieved during the course of the experiments. Chemistry data for the propylene + NO_x system and chemistry and aerosol data for propylene + NO_x + SO_2 tests in which the same initial reactant concentrations were used are plotted in Figures 2-5 (i.e., run numbers 15, 16 and 22, 23).

From the data in Table IV, it can be seen that for an initial concentration of 3.0 ppmC propylene and 0.50 NO_x (runs 15, 16, 22, and 23), the time to ozone peak is about 180 to 190 minutes, and the time to NO_2 max is about 120 minutes. The Battelle data is similar, but the time to $[NO_2]_{max}$ is somewhat shorter. Maximum ozone concentrations are between .550 and .705 ppm for the Calspan runs and about .420 ppm for the Battelle tests. Variations in the initial reactant concentrations resulted in appreciable differences in the ozone (max), as well as in the times to O_3 and NO_2 maxima. The addition of SO_2 to the propylene + NO_x system did not affect the chemical behavior in any significant manner. A somewhat reduced $[O_3]_{max}$ yield in the presence of SO_2 may be inferred from the Calspan data, but a definitive conclusion to this effect cannot be made.

Table IV.

SUMMARY OF CHEMISTRY DATA FROM PROPYLENE + NO_x AND PROPYLENE + NO_x + SO_2 IRRADIATIONS

Run No.	Date	System	Propylene ppmC	NO_i ppm	NO_{2i} ppm	$[O_3]_{max}$ ppm	Time to $[O_3]_{max}$ min	Time to $[NO_2]_{max}$ min
11	10/21/74	Propylene + NO_x	3.0	0.46	.13	.760	140	85
14	12/27/74	"	3.0	0.60	.05	.790	235	150
15	12/31/74	"	3.0	0.46	.04	.705	180	110
16	1/03/75	"	3.0	0.45	.05	.685	190	120
Battelle - 114		"	2.9	0.42	.10	.420	190	85
17	1/16/75	Propylene + NO_x + SO_2	3.5	0.48	.05	.605	135	95
21	2/14/75	"	2.6	0.48	.04	.555	225	165
22	2/16/75	"	3.1	0.46	.03	.555	180	120
23	2/17/75	"	3.1	0.47	.05	.565	180	120
Battelle - 197		"	3.2	0.39	.10	.430	160	60

Table V.

SUMMARY OF AEROSOL DATA FROM PROPYLENE + NO_x AND PROPYLENE + NO_x + SO_2 IRRADIATIONS

Run No.	Date	System	N_{max} cm^{-3}	$[\frac{dv}{dt}]_{SO_2}$ $\mu m^3/cc\text{-}hr$	$R_{SO_2(initial)}$ $\%\ hr^{-1}$	$[\frac{dv}{dt}]_{max}$ $\mu m^3/cc\text{-}hr$
11	10/21/74	Propylene + NO_x	2.6×10^5	--	---	6.1
14	12/27/74	"	1.0×10^5	--	---	--
15	12/31/74	"	1.4×10^5	--	---	--
16	1/03/75	"	1.2×10^5	--	---	--
Battelle - 114		"	--	--	---	--
17	1/16/75	Propylene + NO_x + SO_2	$>10^7$	18.1	0.7	>1500
21	2/14/75	"	4.0×10^6	3.2	0.3	466
22	2/16/75	"	$>10^7$	5.3	0.4	392
23	2/17/75	"	$>10^7$	4.7	0.4	361
Battelle - 197		"	9.5×10^5	23.0	0.7	77

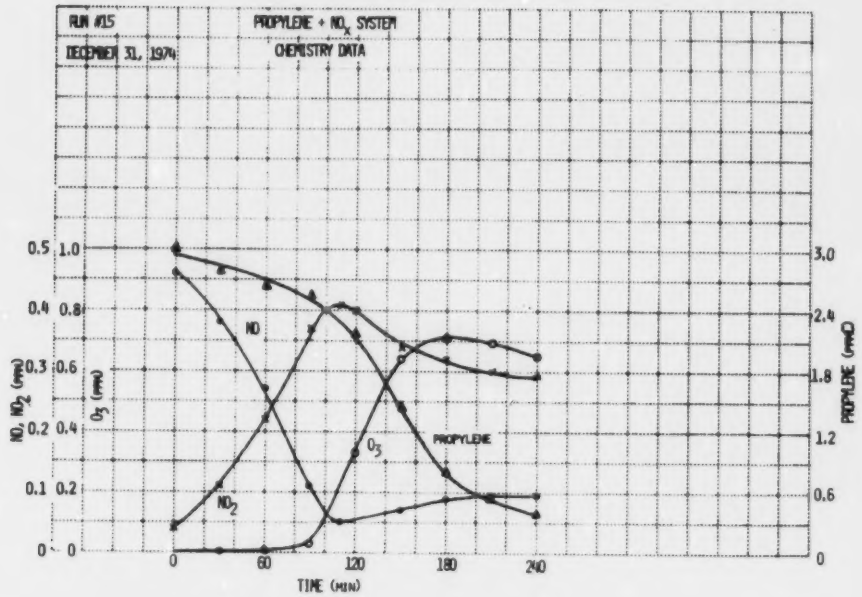

Figure 2 CHEMISTRY DATA FOR PROPYLENE + NO_X SYSTEM

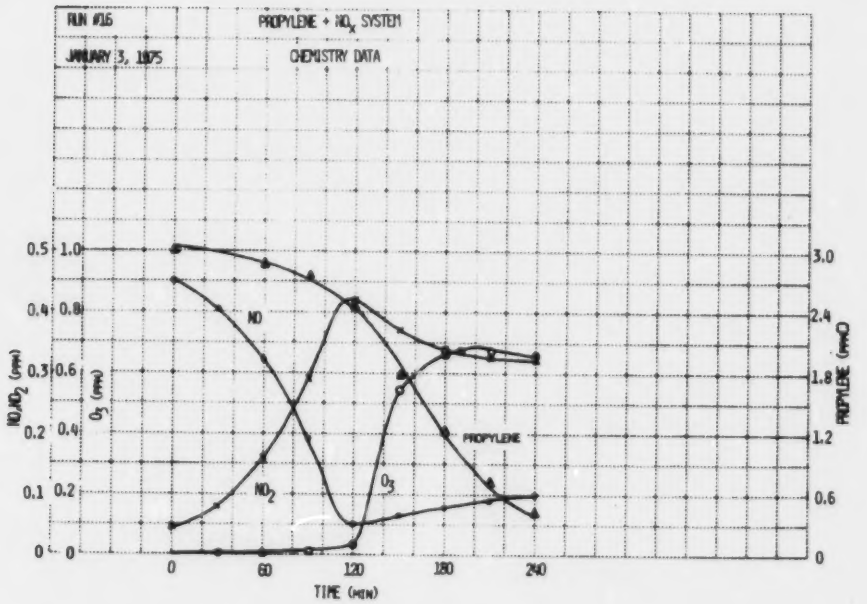

Figure 3 CHEMISTRY DATA FOR PROPYLENE + NO_X SYSTEM

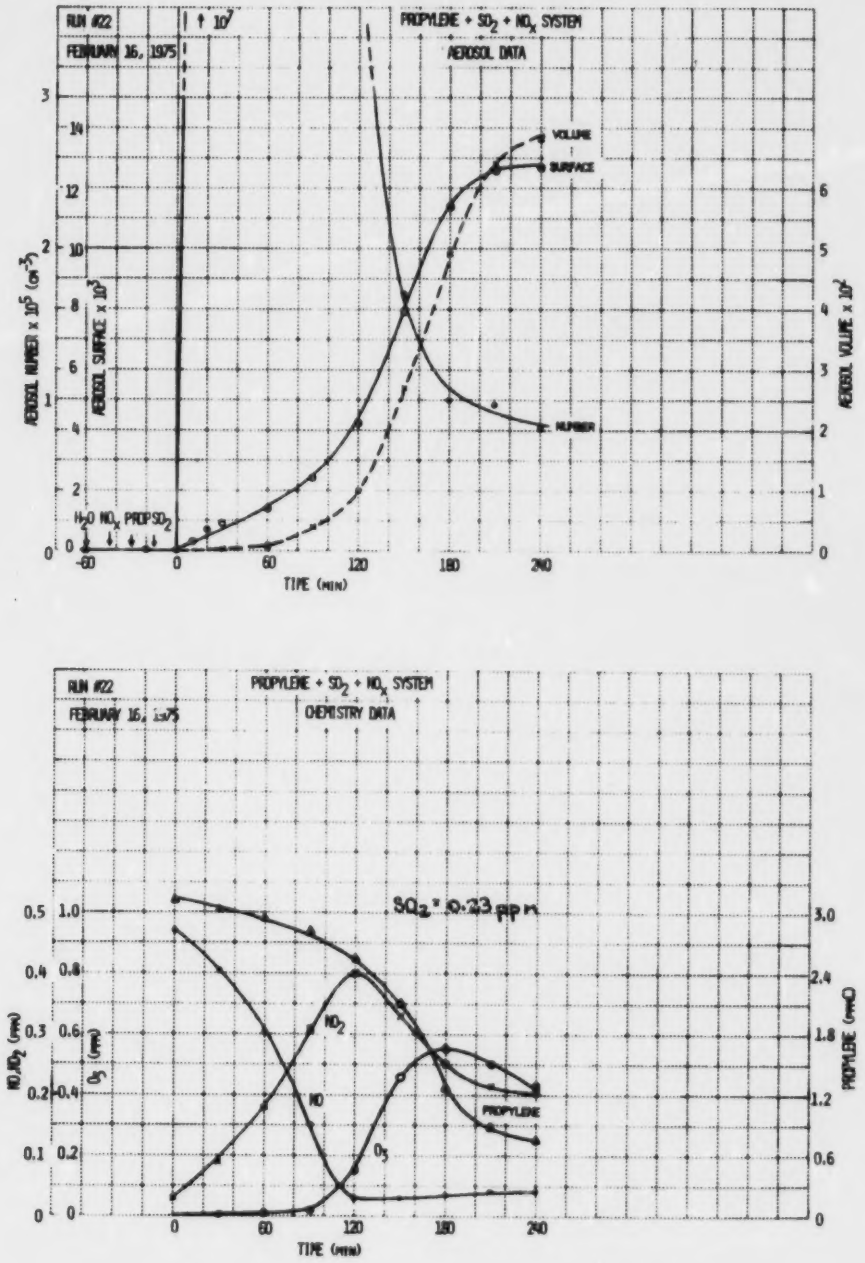

Figure 4 AEROSOL AND CHEMISTRY DATA FOR PROPYLENE + NO_X + SO_2 SYSTEM

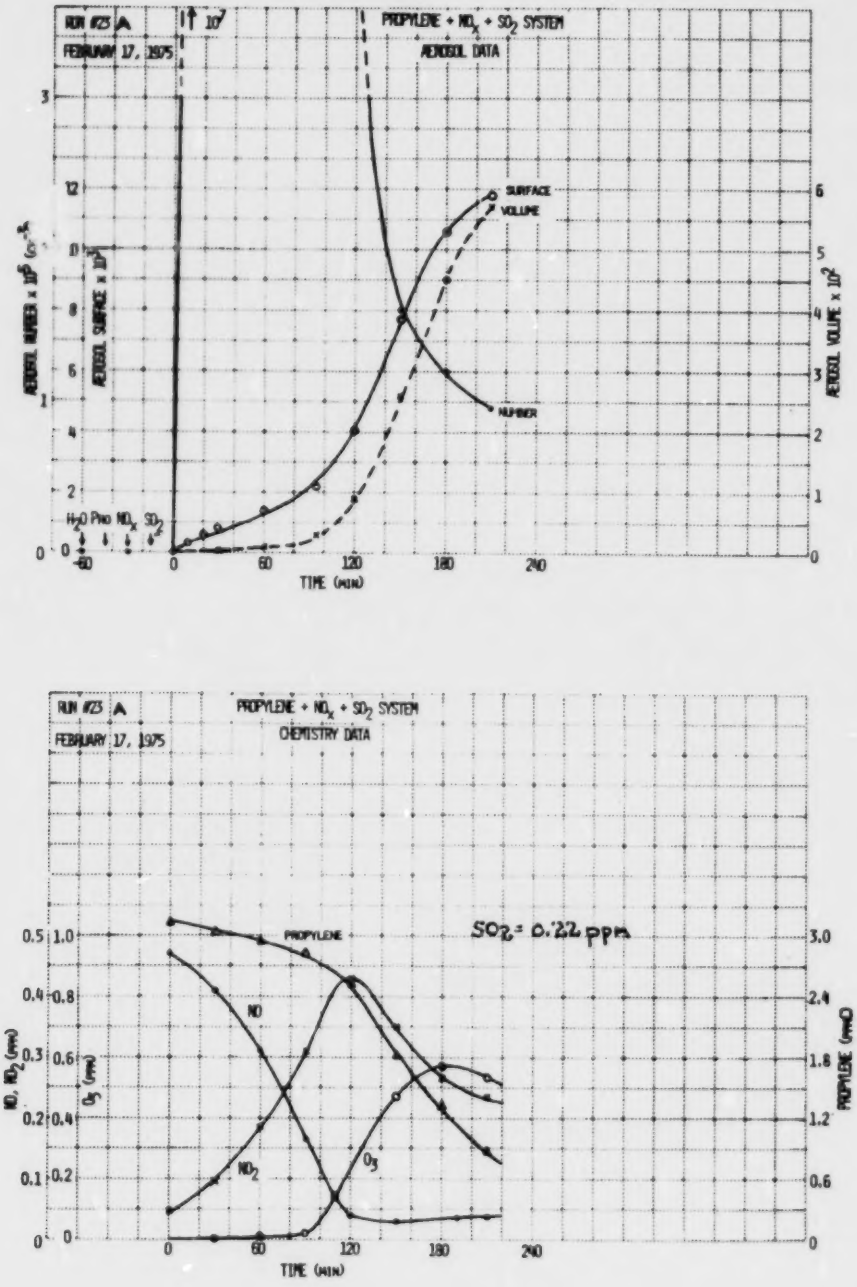

Figure 5 AEROSOL AND CHEMISTRY DATA FOR PROPYLENE + NO_X + SO_2 SYSTEM

By contrast, large differences were noted in aerosol behavior of the propylene + NO_x system after adding SO_2. The most obvious differences observed were in the peak number concentration and maximum volumetric growth rate of the aerosol. The data in Table V show that the maximum particle concentration was generally more than two orders of magnitude greater for the propylene + NO_x system with added SO_2. A malfunction of the aerosol analyzer during experiments 14-16 prevented the acquisition of aerosol data for these experiments. In experiment 11, the [dv/dt]max for the propylene + NO_x system in the absence of SO_2 was found to be 6.1 $\mu m^3/cc\text{-}hr^{-1}$. An apparent synergistic effect seems to occur with the addition of SO_2 in that the maximum volumetric growth rate is greater for the mixed system than for the individual rates of propylene + NO_x and SO_2 combined. Note that [dv/dt]max for experiments 17-23 in which there was added SO_2 produced volumetric growth rates which ranged from 361 to >1500 $\mu m^3/cc\text{-}hr^{-1}$. Before the onset of rapid O_3 formation, the volumetric growth rate was more like that of the SO_2 + clean air system alone (i.e., a few $\mu m^3/cc\text{-}hr^{-1}$). The computed R_{SO_2} for the first 30 minutes of experiments 17-23 was between 0.3 and 0.7% hr^{-1}.

Some of these features can be seen from the aerosol data plotted in Figures 4 and 5 (experiments 22 and 23) for the propylene + NO_x + SO_2 system. After admitting SO_2 and irradiating the sample, there was an expected rise in particle concentration to values in excess of 10^7 cc^{-1}. The volume concentration during the first 60 to 90 minutes was very low because of the small size of the nuclei, generally less than 0.04 μm in diameter.

The beginning of the second stage of aerosol growth occurred at about the time that the NO was oxidized out of the system and rapid O_3 formation took place. At this point (about 110 minutes), there was a seemingly explosive growth of the aerosol in terms of both surface and volume concentrations. Nearly all of the growth was in the form of additional condensation on existing particles since the particle concentration did not increase during this period. By contrast, in the propylene + NO_x system, only a modest increase in particle number occurred after NO oxidation was complete. Some aerosol growth occurs, but it is small compared to that observed for the system with added SO_2.

At Battelle, kinetic treatment of the data indicates that during the induction period (when the NO/NO_2 ratio >1), oxidation of SO_2 to aerosol can be attributed entirely to the SO_2 + OH reaction. Oxidation of SO_2 is relatively slow during this period because of the competition for OH exhibited by propylene and NO_x. Estimates suggest that only 1-2 percent of the OH during this period is available to react with SO_2. It may also be inferred for this interval that the rate of SO_2 oxidation by HO_2 and RO_2 is at least two orders of magnitude slower than the rate of NO oxidation by these intermediates.

About the time of O_3 appearance, there is a rapid rise in the rate of SO_2 oxidation. It has not been determined, however, whether the accelerated rate of SO_2 oxidation is due to an increase in OH, RO_2, and HO_2 radicals, or to the appearance of other reactive intermediates resulting from propylene + O_3 reactions.

Although sulfate analyses had not started at Calspan when these experiments were performed, more recent determinations show that the average SO_2 photooxidation rate during the overall irradiation period in the propylene + NO_x + SO_2 system is approximately 2.7% hr^{-1}. For Battelle run #107, the maximum rate is about 2.3%/hr which is in accord with the Calspan data. (Recall that R_{SO_2} is typically about one percent per hour for the SO_2 + clean air system.) Since the accelerated production of aerosol during the second growth stage amounts to an equivalent SO_2 photooxidation rate of up to 30% hr^{-1}, most of the aerosol which is produced must be organic in nature. Additional determinations of sulfate concentration in the HC-NO_x-SO_2 system are planned both at Calspan and Battelle in an effort to establish the conditions of maximum SO_2 photooxidation rate and to assess in more detail the chemical nature of aerosol composition.

Section 5

THE INORGANIC SYSTEM - $CO + NO_x + SO_2$

One of the questions regarding the rate of SO_2 photooxidation involves the contributions of the HO and HO_2 radicals to the overall oxidation process. Theoretically, if contaminants leading to the formation of OH are important, then one should be able to study the effects of OH scavenging on R_{SO_2} by irradiating an inorganic system such as $CO + NO_x + SO_2$. It is postulated that the added CO would scavenge OH radicals in competition with SO_2 and thus inhibit the oxidation of SO_2. The higher the CO level the lower would be the expected oxidation rate of SO_2. In the postulated competitive process for OH radicals, the following reactions involving OH and HO_2 are expected to be important:

$$HO + CO \rightarrow CO_2 + H \quad (1)$$

$$H + O_2 + \underline{M} \rightarrow HO_2 + M \quad (2)$$

$$HO_2 + NO \rightarrow HO + NO_2 \quad (3)$$

$$SO_2 + OH(M) \rightarrow HSO_3 \rightarrow \text{Products} \quad (4)$$

At low concentrations of CO, the SO_2 + OH reaction would be a rate controlling process for OH consumption. As the concentration of CO is increased, reaction (1) would become dominant.

In an effort to determine the effects of increasing the level of CO on R_{SO_2}, several experiments were performed in the Calspan chamber using various levels of CO ranging from background concentrations to about 400 ppm. The NO and NO_2 concentrations were kept at approximately 0.5 ppm and 0.05 ppm respectively. The average temperature for the tests was ~80°F and the relative humidity was kept as close as possible to 50%. Chemistry and aerosol data for these experiments are summarized in Tables VI and VII.

Table VI.

SUMMARY OF CHEMISTRY DATA FROM THE INORGANIC TEST SERIES

Run No.	Date	System	CO_i ppm	NO_i ppm	NO_{2i} ppm	SO_{2i} ppm	$O_{3\ max}$ ppm
27	4/08/75	$SO_2 + NO_x$ + b (CO)	b*	0.52	0.05	0.55	.002
28	4/09/75	$SO_2 + NO_x$ + b (CO)	b	0.51	0.05	0.72	.002
29	4/10/75	$SO_2 + NO_x$ + b (CO)	b	0.46	0.04	0.56	.002
31	4/14/75	$SO_2 + NO_x$ + CO	100	0.43	0.03	0.60	.046 ↑
33	4/18/75	$SO_2 + NO_x$ + CO	100	0.42	0.03	0.56	.031 ↑
34	4/22/75	$SO_2 + NO_x$ + CO	430	0.46	0.04	0.44	.520 ↑
36	4/29/75	$SO_2 + NO_x$ + CO	410	0.62	0.06	0.48	.267 ↑

*Background level of CO; generally <1 ppm

Table VII.

SUMMARY OF AEROSOL DATA FROM INORGANIC TEST SERIES

Run No.	Date	System	N_{max} cc^{-1}	S_{max}* $\mu m^2/cc$	$R_{SO_{2(i)}}$ % hr^{-1}	$R_{SO_{2(max)}}$ % hr^{-1}	$R_{SO_{2(ave)}}$ % hr^{-1}
27	4/08/75	$SO_2 + NO_x$ + b (CO)	$>10^7$	3.2×10^3	0.6	1.1	0.8
28	4/09/75	$SO_2 + NO_x$ + b (CO)	$>10^7$	3.4×10^3	0.4	0.9	0.8
29	4/10/75	$SO_2 + NO_x$ + b (CO)	$>10^7$	3.2×10^3	0.5	1.6	1.0
31	4/14/75	$SO_2 + NO_x$ + CO	$>10^7$	2.9×10^3	0.3	0.9	0.6
33	4/18/75	$SO_2 + NO_x$ + CO	$>10^7$	2.6×10^3	0.4	1.0	0.6
34	4/22/75	$SO_2 + NO_x$ + CO	$>10^7$	2.9×10^3	0.5	1.1	0.8
36	4/29/75	$SO_2 + NO_x$ + CO	$>10^7$	3.2×10^3	0.3	1.2	0.8

*$S_{(max)}$ = maximum surface area of aerosol produced during experiment.

The data show that in the Calspan chamber neither the initial nor the maximum SO_2 photooxidation rate is affected by changes in the CO concentration up to 400 ppm when there is appreciable NO_x in the system. There are, however, changes which occur with respect to the chemistry. As the CO level is increased, there is a noticeably more rapid oxidation of NO to NO_2 together with an increase in the amount of ozone formed. Representative illustrations of chemistry and aerosol data for each of three CO levels (background, 100 ppm and 400 ppm) are shown in Figures 6, 7, and 8.

The figures show that aerosol behavior is nearly identical for the three CO levels tested. The principal difference in the tests was in the larger dark reaction in the experiments involving high concentrations of CO. (Dark reactions could be minimized by introducing the CO into the chamber through a charcoal + Al_2O_3 scrubber to remove metal carbonyl contaminants.) As shown for each test, there is an immediate rise in particle concentration after turning on the lights. The maximum number always exceeded the upper limit (10^7 particles/cc) of the Gardner small particle detector at this stage of this experiment. After periods of time ranging from less than 10 minutes to about an hour, the concentration of particles decreased to a level within the range of the particle detector. Meanwhile, the aerosol surface and volume concentrations increase slowly at first and then at a slightly more rapid rate. For these experiments the range of initial SO_2 oxidation rates was between 0.3 and 0.6% hr^{-1} or approximately the same as that measured for the SO_2 + clean air system. The average SO_2 oxidation rate, $R_{SO_2(ave)}$, as measured with the aerosol analyzer was in the range of 0.6 to 1.0 hr^{-1}, which is somewhat lower than in the SO_2 + clean air system. No changes are evidenced in the aerosol data as a function of the increasing CO concentration. The maximum particle concentration, N_{max}, and the maximum aerosol surface concentration, S_{max}, is approximately the same for all seven experiments.

This series of experiments was conducted in the absence of any hydrocarbon additives. The fate of OH and HO_2 radicals within the reaction system was largely governed by the presence of NO and NO_2 as shown by Reaction (3).

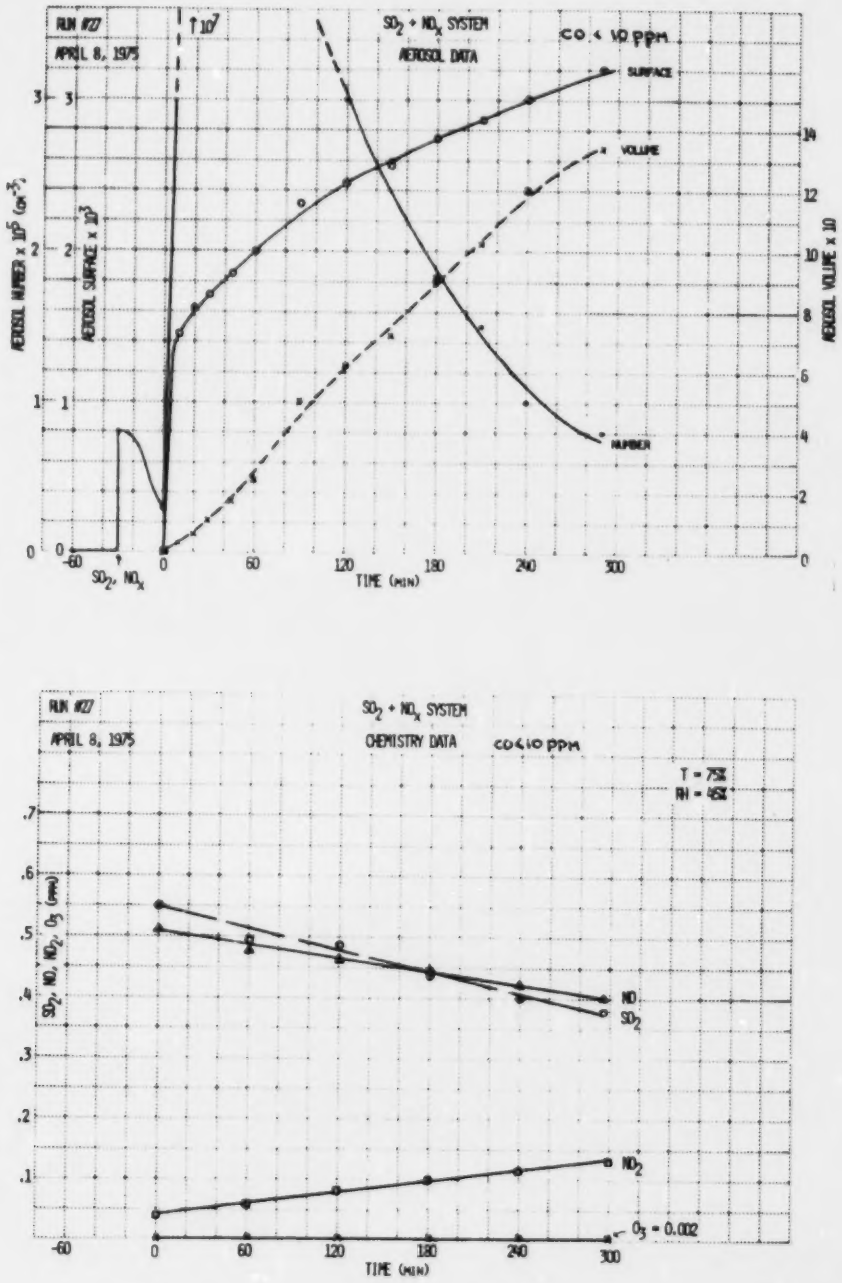

Figure 6 AEROSOL AND CHEMISTRY DATA FOR SO_2 + NO_X SYSTEM

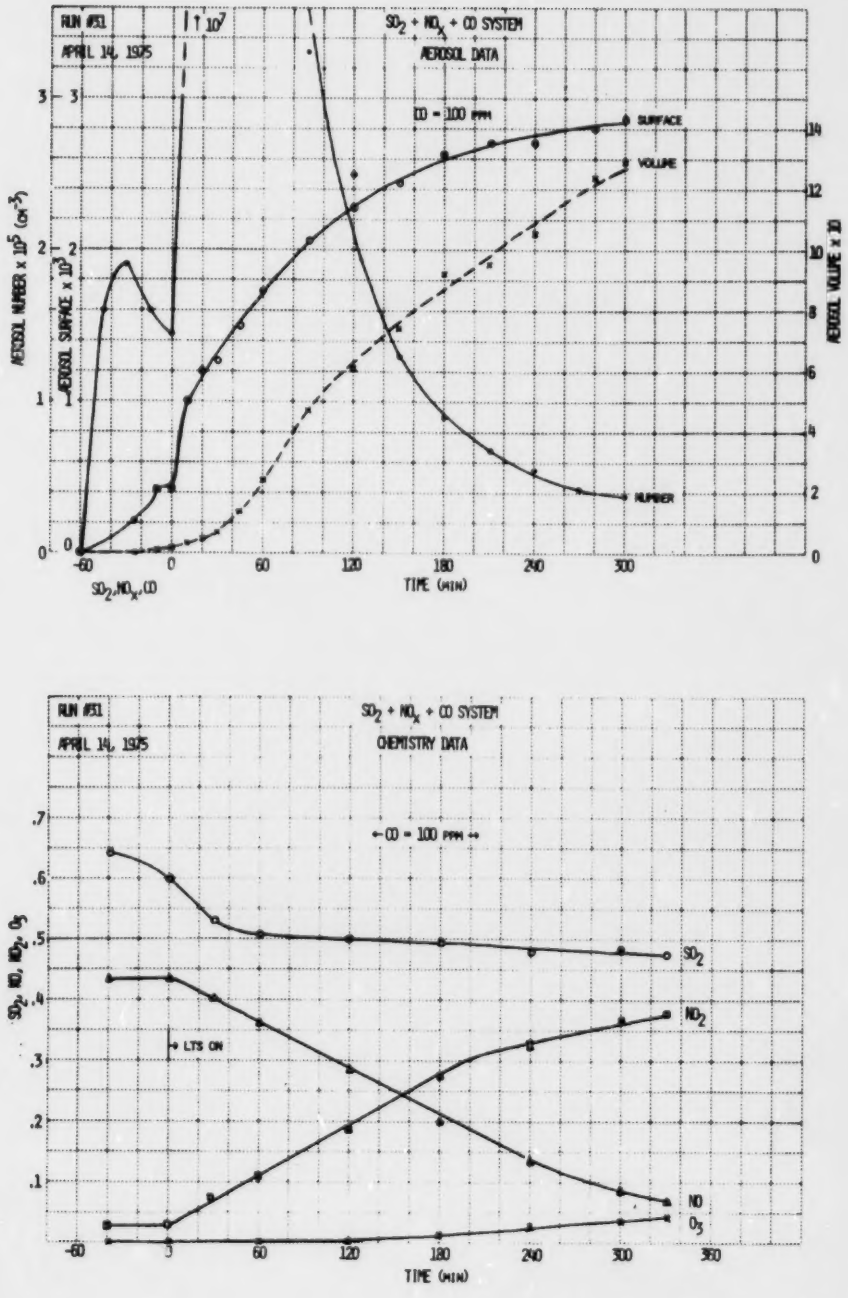

Figure 7 AEROSOL AND CHEMISTRY DATA FOR SO_2 + NO_X + 100 PPM CO SYSTEM

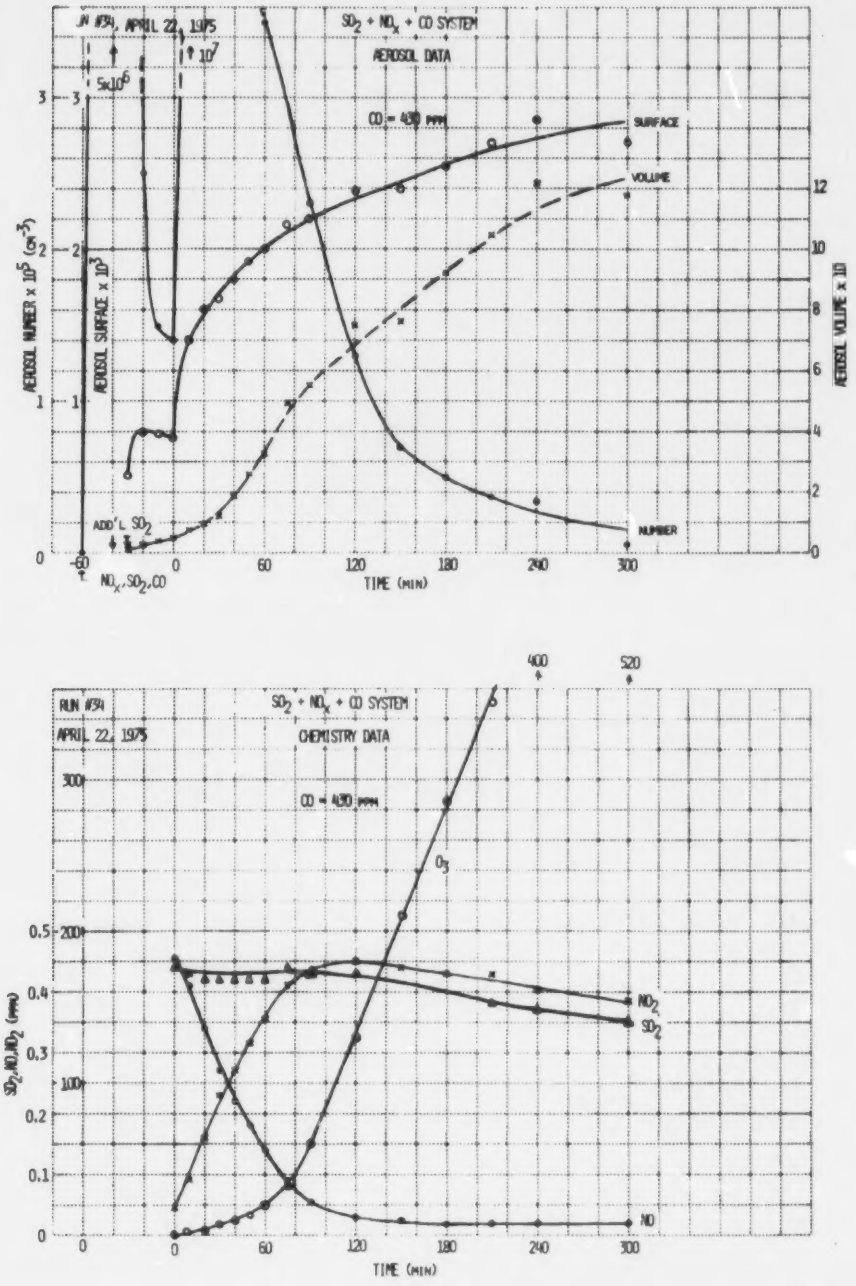

Figure 8 AEROSOL AND CHEMISTRY DATA FOR SO_2 + NO_X + 400 PPM CO SYSTEM

The observed data showing a lack of effect of added CO up to 400 ppm is therefore consistent with the expectation that the rate of Reaction (1) is small in comparison to the reverse rate of Reaction (3). The results of the above experiments are not conclusive, since sulfate analysis from aerosol collections were only in agreement with the <u>initial</u> rate of SO_2 oxidation in the clean air + SO_2 experiments. As mentioned previously, it is possible that the final rate of SO_2 oxidation as determined from the EAA may be erroneously high due to the contributions to aerosol growth from reactions other than those involving sulfate. If this is the case, the $R_{SO_{2(ave)}}$ may actually be even lower than that shown. Additional experiments are needed to resolve this question.

Section 6

THE RURAL AIR + SO_2 SYSTEM

A few experiments were performed to examine possible catalytic effects of natural nuclei in rural air on the SO_2 oxidation rate. These tests were preliminary in nature and are still under way so that only a brief discussion of results will be presented here. Some results have already been presented in Section 3 as part of the comparison of sulfate analysis procedures using the EAA data and the barium perchlorate method.

Chemistry and aerosol data for the rural air, rural air + SO_2, and filtered rural air (free of particles only) + SO_2 systems are shown in Table VIII. The table shows the run number and conditions, initial SO_2 concentration, sulfate content, R_{SO_2} as determined from sulfate analysis, the maximum aerosol surface concentration, and the NH_4^+ content of the aerosol samples. In our previous discussion, we stated that the SO_2 photooxidation rate as computed from aerosol sulfate data was found to fall within the range of 0.3 to 0.5 percent per hour regardless of whether the SO_2 was irradiated in natural rural air, with only the natural particles removed, or with cleaning through absolute plus charcoal filtering of air. Initial aerosol growth was found to be somewhat enhanced over the SO_2 + clean air system, but for the most part aerosol development was similar for both systems.

Three classes of rural air experiments were performed. They are summarized in Table VIII and illustrated in Figures 9, 10, and 11. The first experiment set, numbers 42, 43 and 44, involves irradiations of rural air alone with no other added contaminants. Data from these experiments provide a baseline against which the rural air + SO_2 experiments can be compared. As shown in Figure 9, no appreciable aerosol development occurs in the "simple" rural air system. In the absence of SO_2, only modest increases are noted in aerosol number, surface and volume concentrations after the lights are turned on. Some small sulfate content was measured in the aerosol sample (~0.5 $\mu g/m^3$,

Table VIII. AEROSOL SAMPLE SULFATE AND AMMONIUM CONTENT

Run No. & Conditions	Initial SO_2 Conc., ppm	Sulfate Content $\mu g/m^3$	SO_2 Ox. Rate, % hr	R_{SO_2}(initial) EAA Data % hr	R_{SO_2}(max) EAA Data % hr	NH_4^+ Content $\mu g/m^3$	S(max) $\mu m^2/cc$
42 Rural air	<0.01	.53	0	0	0	0	500
43 Rural air (filtered)	<0.01	.67	0	0	0	0	100
44 Rural air (filtered)	<0.01	4.9	0	0	0	8.1	190
46 SO_2 + rural air	0.52	35.2	0.5	2.0	2.3 +	17.2	3400
47 SO_2 + rural air	0.48	25.2	0.4	1.2	1.6 +	17.7	3200
48 SO_2 + rural air	0.52	23.6	0.3	1.0	1.4 +	15.7	3700
51 SO_2 + filtered rural air	0.65	25.5	0.3	1.9 +	(Dark Rx)	16.5	3400
52 SO_2 + filtered rural air	0.50	49.3	0.7	0.8	1.1	15.4	2500
53 SO_2 + filtered rural air	0.54	22.8	0.3	1.1	1.2	13.1	2600

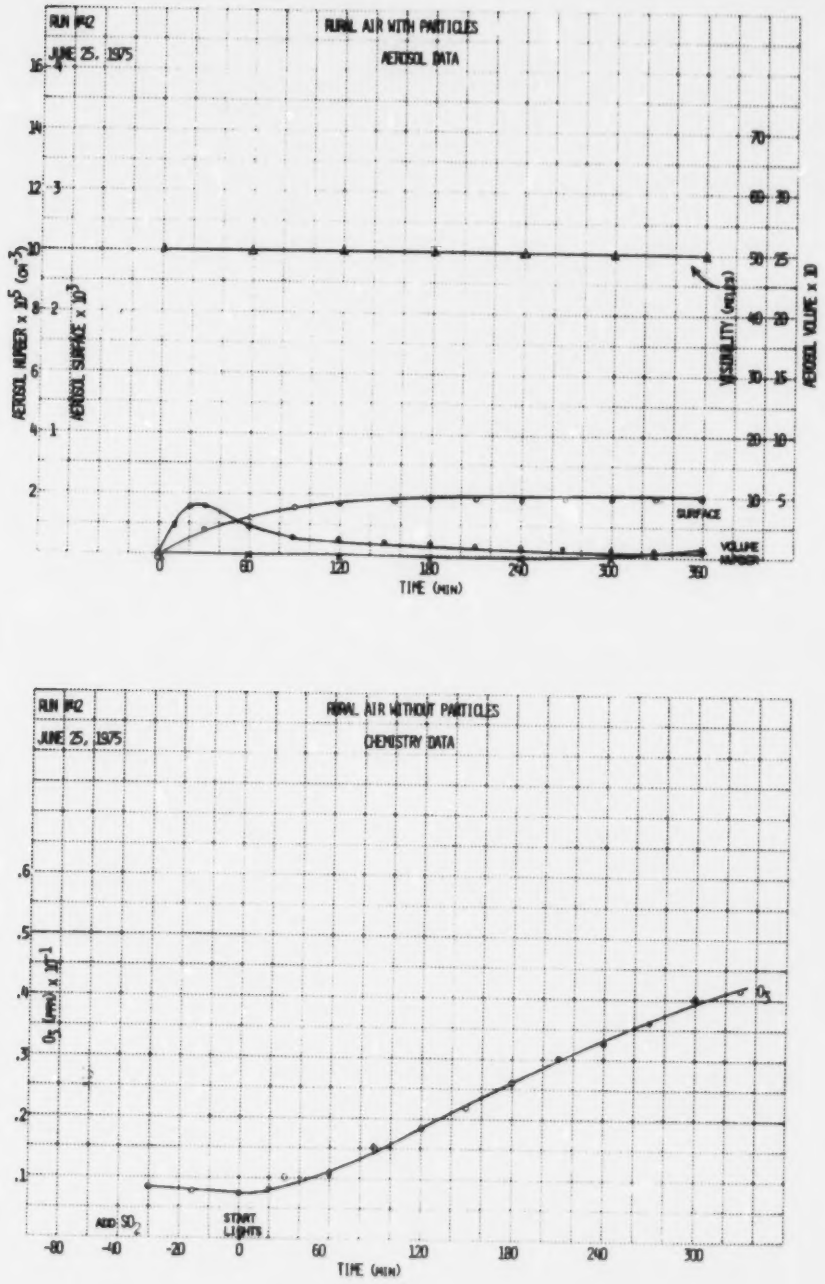

Figure 9 AEROSOL AND CHEMISTRY DATA FOR RURAL AIR SYSTEM CONTAINING NATURAL PARTICLES

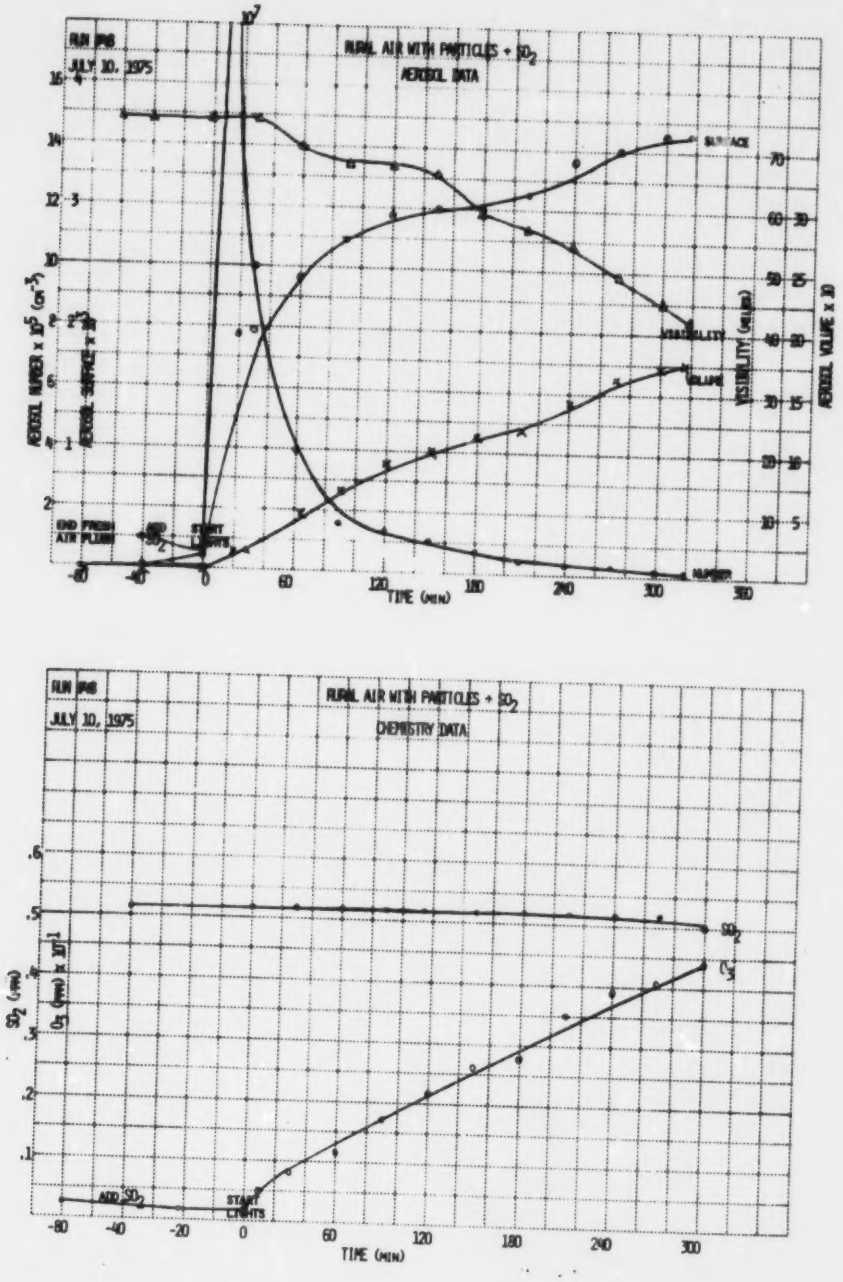

Figure 10 AEROSOL AND CHEMISTRY DATA FOR RURAL AIR (WITH NATURAL PARTICLES) + SO_2 SYSTEM

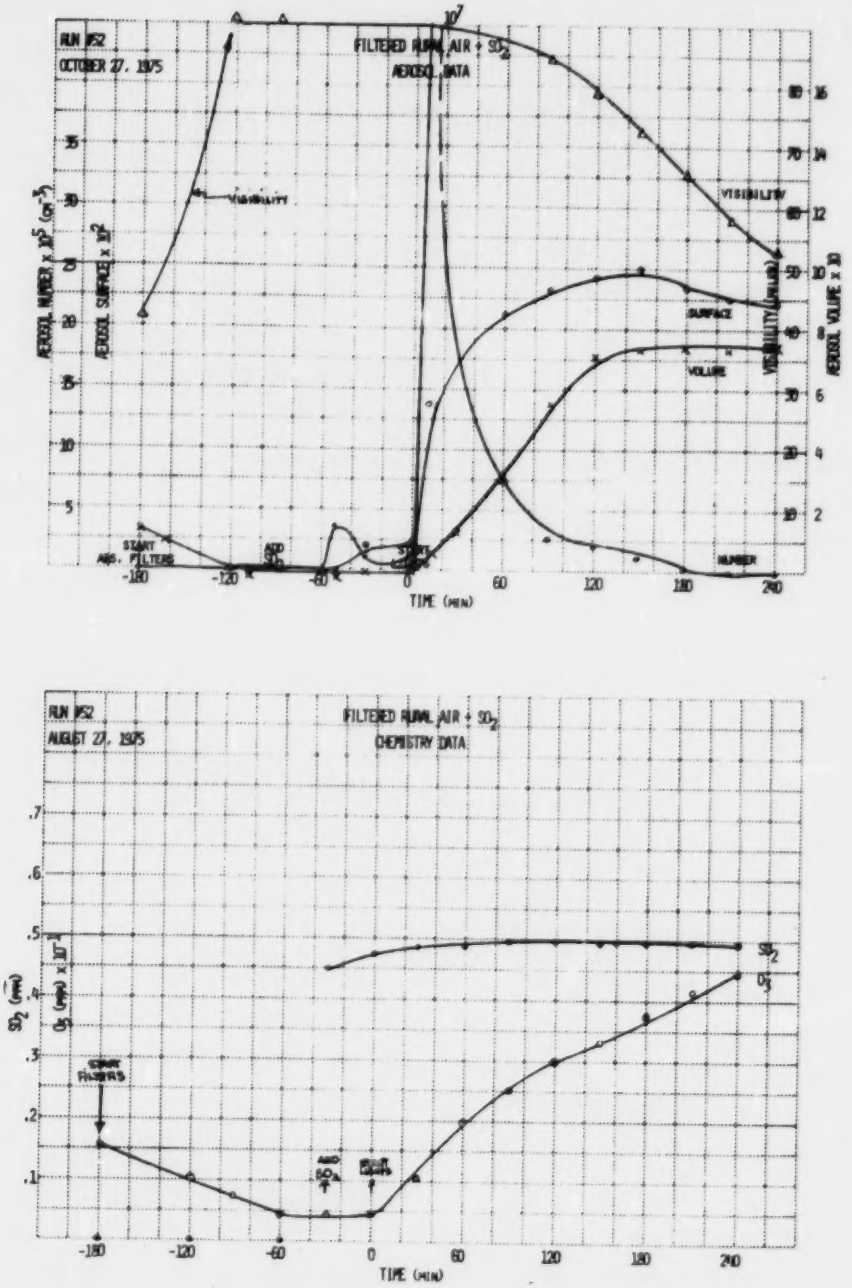

Figure 11 AEROSOL AND CHEMISTRY DATA FOR RURAL AIR (WITHOUT NATURAL PARTICLES) + SO_2 SYSTEM

Table VIII) and also NH_4^+ (~8 $\mu g/m^3$); however, these concentrations are considered normal for a relatively contamination-free environment.

In experiments 46, 47 and 48, SO_2 was added to unfiltered rural air and irradiated for several hours. In these experiments substantial aerosol growth in excess of either the SO_2 + clean air or the rural air system was observed. The newly formed aerosol is not pure H_2SO_4, however, since results of the sulfate analysis indicate an SO_2 oxidation rate of 0.3 to 0.5% hr^{-1}. This is substantially below the 1.0 to 2.0% hr^{-1} (as determined from EAA analysis) which would be necessary to account for all the aerosol that is produced. An example of this type of system is shown in Figure 10. The figure shows typical features of aerosol development for photochemical systems involving SO_2. The principal difference between this and most other systems is the more rapid aerosol volume and surface development during the first 60 minutes or so of the experiment. In most SO_2 + clean air experiments, there is a slow initial aerosol growth followed by somewhat accelerated rates after the first 30 minutes of irradiation. On the other hand, in the rural air + SO_2 experiments, there was a slight decrease in aerosol volume late in the experiment, presumably because aerosol growth had proceeded beyond the detection range of the EAA, resulting in an "apparent" aerosol loss.

In the final test series of the rural air experiments, SO_2 was introduced into the chamber after first removing all natural particles from the system. In this sense, the system was similar to the SO_2 + clean air system except that natural rural background levels of NO_x, HC and ozone were present in the chamber air. Aerosol and chemistry data from this type of system is illustrated in Figure 11. In this test series, R_{SO_2} as determined from sulfate analysis was not affected to any large extent by the presence of natural background impurities. Although initial aerosol surface and volume growth is slightly higher in this system than for SO_2 + clean air alone, the differences are not large and are not considered significant.

Section 7

SUMMARY AND CONCLUSIONS

Over 54 experiments were performed during the past year to gather smog chamber irradiation data on various systems ranging from SO_2 in clean air to CO + NO_x + SO_2 experiments and rural air + SO_2 irradiations. From an analysis of the aerosol and chemistry data generated in these systems, the following conclusions can be made:

(1) The average SO_2 photooxidation rate in the Calspan chamber is approximately 1.0% hr^{-1} in clean filtered air. Sulfate determinations from aerosol analysis by the barium perchlorate method were in good agreement with EAA data during the initial phases of aerosol development. Determinations of R_{SO_2} from EAA data were generally higher during the later stages of the experiment.

(2) In the presence of hydrocarbon contamination (in this case, propylene), higher rates of SO_2 oxidation are observed. Recent data points to an average R_{SO_2} in the propylene + NO_x + SO_2 system of about 2.7% hr^{-1}.

(3) Apparent synergistic effects occur with the addition of SO_2 to the propylene + NO_x system in that the maximum volumetric growth rate of aerosol is greater for the mixed system than the sum of rates for propylene + NO_x and SO_2 alone. Abundant production of aerosol during the maximum growth phase may be attributed in part to the formation of non-sulfate particulates probably organic in nature.

(4) Using concentration of 3.0 ppmC propylene, 0.50 NO_x, and a light intensity of $k_d[NO_2]$~0.35 min^{-1}, the time to ozone peak is about 180 minutes, and the time to NO_2 maximum is about 120 minutes in the Calspan chamber. Although maximum ozone yields appeared somewhat lower for the SO_2

containing system, overall chemistry data for the propylene + NO_x system with or without the addition of SO_2 were basically similar.*

(5) Experiments using an inorganic test system of CO + NO_x + SO_2 shows no appreciable difference in R_{SO_2} as a function of CO concentration when there is excess NO_x present. Amounts of CO ranging from <10 ppm to 400 ppm were used in the tests. In recent irradiations using SO_2 clean air, it has been observed that the addition of CO (60 ppm) appreciably lowers the SO_2 photooxidation rate. These observations are consistent with the presumed mechanism that the OH-SO_2 reaction is mainly responsible for SO_2 photooxidation. A competitive OH radical scavenging by added CO via

*As shown by data in Table IV, the time to $[O_3]_{max}$ is very sensitive to the initial $[HC]/[NO_x]$ ratio, while the $[O_3]_{max}$ achieved during irradiation is dependent on the initial $[NO_x]$. In experiments with comparable $[NO_x]_i$ at about 0.5 ppm, a somewhat lower $[O_3]_{max}$ associated with the presence of SO_2 is consistently observed. The difference in $[O_3]_{max}$ values in the presence or absence of SO_2 is less than about 20 percent. In kinetic simulation assessments by Niki, Daby and Weinstock (1972) and by Calvert and McQuigg (1975), it has been suggested that a competitive OH radical removal by reactions with CO would result in a lowering of alkylperoxy and acylperoxy radical formation from OH radical reactions with aldehydes and alkenes. This would give rise to slower NO to NO_2 conversion with a consequent lowering of the O_3 yield. By analogy, one may expect the presence of SO_2 to exert a similar effect as indicated by our data in Table IV. On the other hand, the production of significantly higher aerosol yields in the SO_2-containing systems or just the later dates of irradiation experiments may have entailed a slightly lower light intensity in these latter cases. This would account for a lower $[O_3]_{max}$ without significantly affecting other aspects of chemical changes. In view of these uncertainties and the fact that a corresponding decrease in $[O_3]_{max}$ was not observed in the Battelle data, definitive conclusions regarding possible SO_2 effects on the HC-NO_x-air irradiation systems would be unwarranted.

$$OH + CO \rightarrow H + CO_2$$

$$H + O_2 + M \rightarrow HO_2 + M$$

would give rise to a reduced R_{SO_2}. In the presence of comparatively high NO, however, OH radical is regenerated by

$$HO_2 + NO \rightarrow OH + NO_2$$

Thus, R_{SO_2} is unaffected by the addition of CO to the $NO_x + SO_2$ + air reaction system. The conversion of NO to NO_2 would, however, be accelerated by the addition of CO.

(6) Results of experiments using particle-free and unfiltered rural air + SO_2 suggest that the photooxidation rate of SO_2 is not affected appreciably by the presence of background levels of natural nuclei. On the other hand, aerosol growth, especially during the early stages of the rural air + SO_2 experiments, is substantially greater than that due to SO_2 photooxidation alone. Other reactions besides those involving sulfate production are probably involved in overall aerosol production. It is recommended that additional experiments be performed to determine the effects of natural and artificial nuclei on the photooxidation rates of SO_2. Special attention in future experiments must be given to aerosol composition analysis in order to assess the role of key constituents on aerosol formation processes.

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APPENDIX A

AEROSOL & CHEMISTRY DATA FOR ALL CALSPAN SMOG CHAMBER EXPERIMENTS

Table A-1. LOG OF CALSPAN SMOG CHAMBER EXPERIMENTS

Run No.	Date	System	Comment	$R_{SO_2(i)}$ % hr^{-1}	$R_{SO_2(max)}$ % hr^{-1}	$R_{SO_2(ave)}$ % hr^{-1}
1	10/11/74	SO_2	Partial lights - chamber not cleaned	1.0	3.6	1.7
2	10/14/74	SO_2	Partial lights - chamber not cleaned	2.9	5.0	4.4
3	10/14/74	Filtered Air	Background check		---	---
4	10/15/74	Filtered Air	Wash chamber - background check		---	---
5	10/16/74	SO_2	Conditioning test	1.3	2.6	1.9
6	10/16/74	SO_2	Conditioning test	0.8	1.7	1.1
7	10/17/74	SO_2	Conditioning test	0.5	1.2	0.9
8	10/17/74	SO_2	Conditioning test	0.2	0.2	0.2
9	10/18/74	SO_2	Conditioning test	0.5	0.7	0.6
10	10/18/74	Propylene + NO	Chamber intercomparison		---	
11	10/21/74	Propylene + NO	Test Series - Exp. 10-23		---	
12	11/14/74	Propylene + NO			---	
13	11/18/74	Propylene + NO			---	
14	12/27/74	Propylene + NO	Begin using HC analyzer		---	
15	12/31/74	Propylene + NO			---	
16	1/03/75	Propylene + NO			---	
17	1/16/75	Propylene+NO+SO_2		0.7	>10%*	
18	2/11/75	SO_2	Begin aerosol collections	0.2	3.0	
19	2/12/75	Propylene+NO+SO_2	ABORT - NO_x Instrument failure		---	
20	2/13/75	Propylene+NO+SO_2	ABORT - NO_x Instrument failure		---	
21	2/14/75	Propylene+NO+SO_2		0.3	>15%*	
22	2/16/75	Propylene+NO+SO_2		0.4	>28%*	
23A	2/17/75	Propylene+NO+SO_2		0.4	>27%*	

*As determined from EAA data. Aerosol undoubtedly contains organic species.

Run No.	Date	System	Comment	$R_{SO_2(i)}$ % hr^{-1}	$R_{SO_2(max)}$ % hr^{-1}	$R_{SO_2(ave)}$ % hr^{-1}
23B	4/04/75	SO_2	Wash chamber - conditioning experiment	11.1	9.7	8.5
24	4/04/75	SO_2	Conditioning experiment	3.4	3.9	3.3
25	4/06/75	SO_2	Conditioning experiment	2.8	2.8	2.5
26	4/07/75	SO_2	Conditioning experiment - SO_2 calibration	3.7	3.7	3.2
27	4/08/75	SO_2+NO_x+b (CO)	Inorganic test series - experiments 27-36	0.6	1.1	0.8
28	4/09/75	SO_2+NO_x+b (CO)		0.4	0.9	0.8
29	4/10/75	SO_2+NO_x+b (CO)		0.5	1.6	1.0
30	4/12/75	SO_2	Background check	0.6	0.9	0.6
31	4/14/75	$SO_2 + NO_x + CO$	100 ppm CO	0.3	0.9	0.6
32	4/17/75	SO_2	Background check	0.5	1.2	1.0
33	4/18/75	$SO_2 + NO_x + CO$	100 ppm CO	0.4	1.0	0.8
34	4/22/75	$SO_2 + NO_x + CO$	400 ppm - Lg. dark reaction	0.5	1.1	0.8
35	4/28/75	$SO_2 + NO_x + CO$	ABORT - Lg. dark reaction		---	
36	4/29/75	$SO_2 + NO_x + CO$	410 ppm CO	0.3	1.2	0.8
37	6/16/75	SO_2	Conditioning experiment $k_d = 0.31$	1.4	4.6	3.0
38	6/20/75	SO_2	Conditioning experiment	0.5	1.7	1.7
39	6/20/75	SO_2	Conditioning experiment	0.7	3.4	1.6
40	6/23/75	SO_2	Conditioning experiment	0.4	2.7	2.1
41	6/24/75	SO_2	Conditioning experiment	0.4	2.7	2.1
42	6/25/75	Rural Air	Irradiation of particle-free rural air		---	
43	6/26/75	Filtered Air	Background check		---	
44	6/30/75	Filtered Air	Background check		---	
45	7/02/75	SO_2	Conditioning experiment	0.5	2.1	1.2
46	7/08/75	Rural Air + SO_2	With natural particles - dark reaction	2.0	2.3 ↓	0.8
47	7/09/75	Rural Air + SO_2	With natural particles	1.2	1.6 ↓	0.8

Run No.	Date	System	Comment	$R_{SO_2(i)}$ % hr^{-1}	$R_{SO_2(max)}$ % hr^{-1}	$R_{SO_2(ave)}$ % hr^{-1}
48	7/10/75	Rural Air + SO_2	With natural particles	1.0	1.4 +	1.1
49	7/17/75	SO_2	Aerosol analyzer calibration	0.5	1.4	0.7
50	8/25/75	SO_2	Background check	0.2	1.6	1.1
51	8/26/75	Particle-Free Rural Air + SO_2	Absolute filtered only	1.9 +		
52	8/27/75	Particle-Free Rural Air + SO_2	Absolute filtered only	0.8	1.1	0.9
53	8/28/75	Particle-Free Rural Air + SO_2	Absolute filtered only	1.1	1.2	0.7
54	8/29/75	SO_2	Background check	0.1	0.9	0.5

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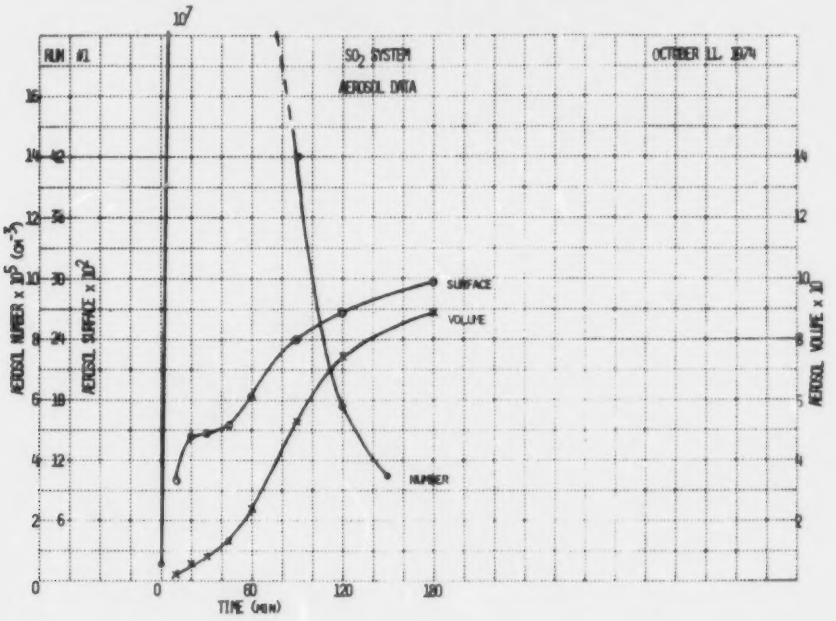

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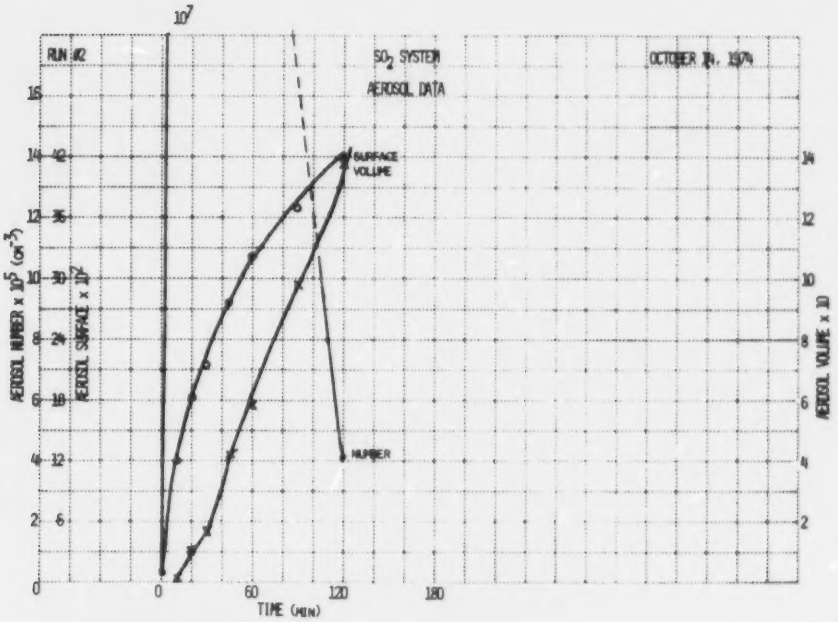

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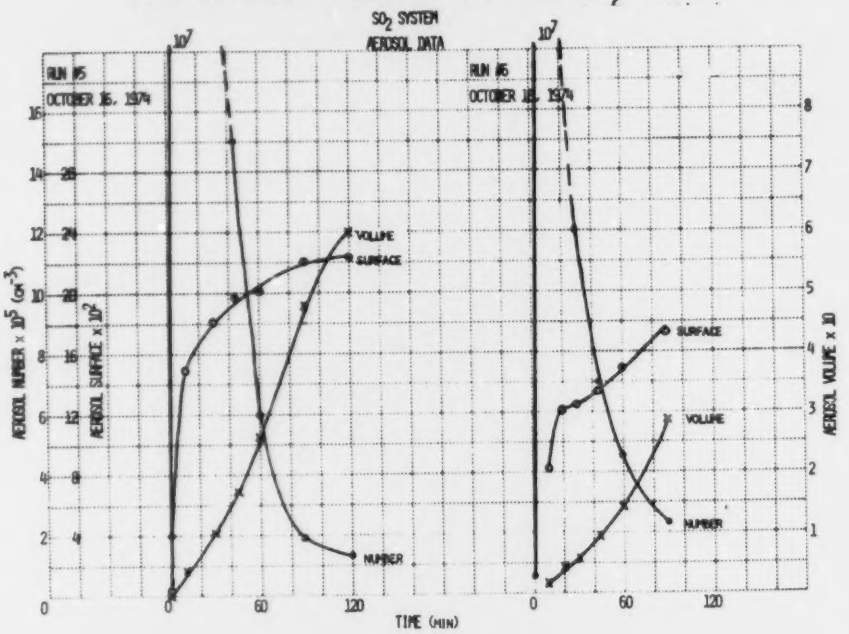

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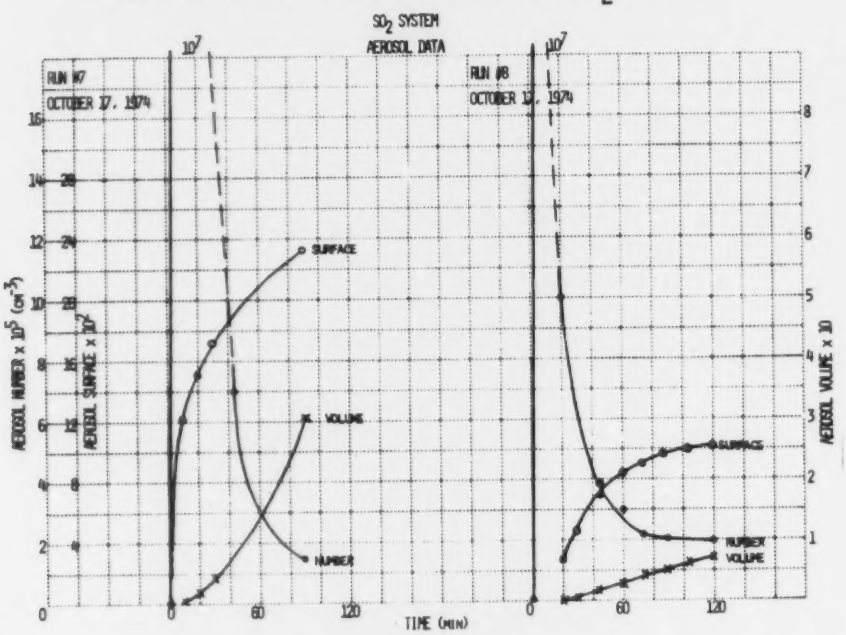

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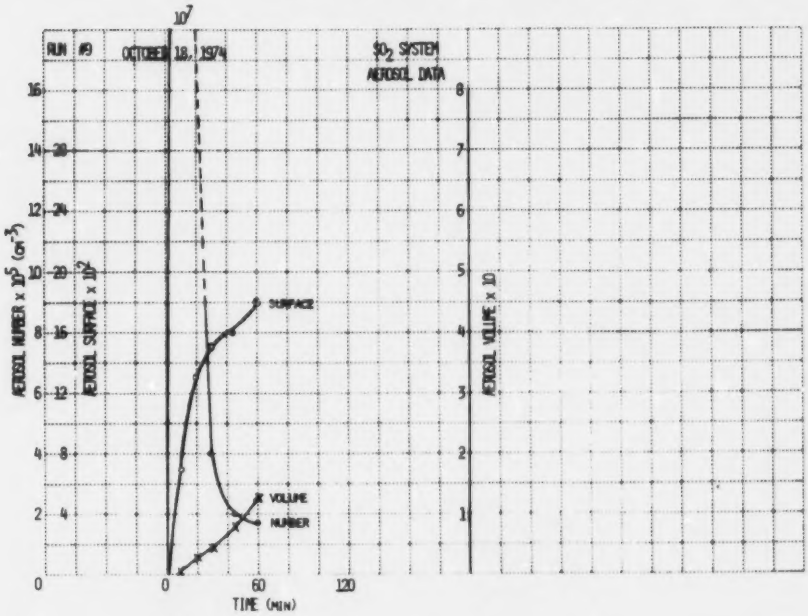

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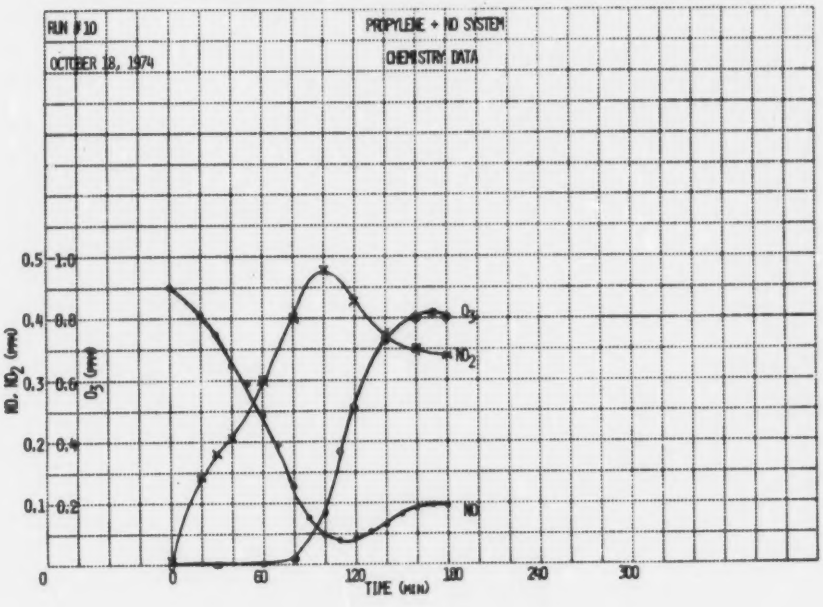

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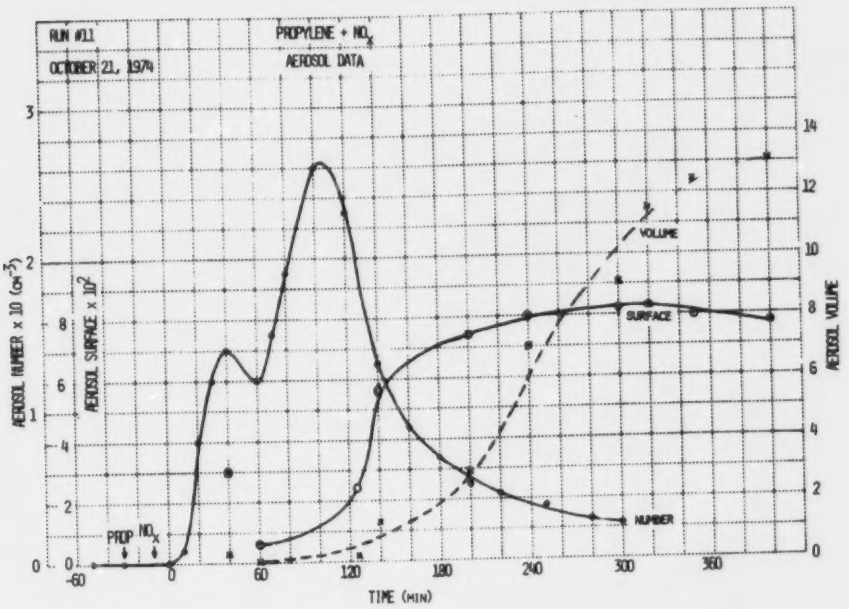

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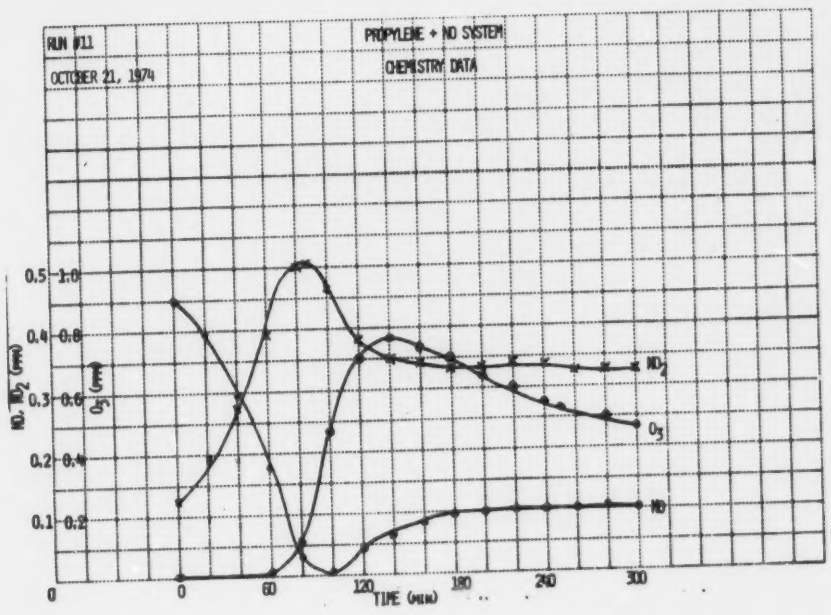

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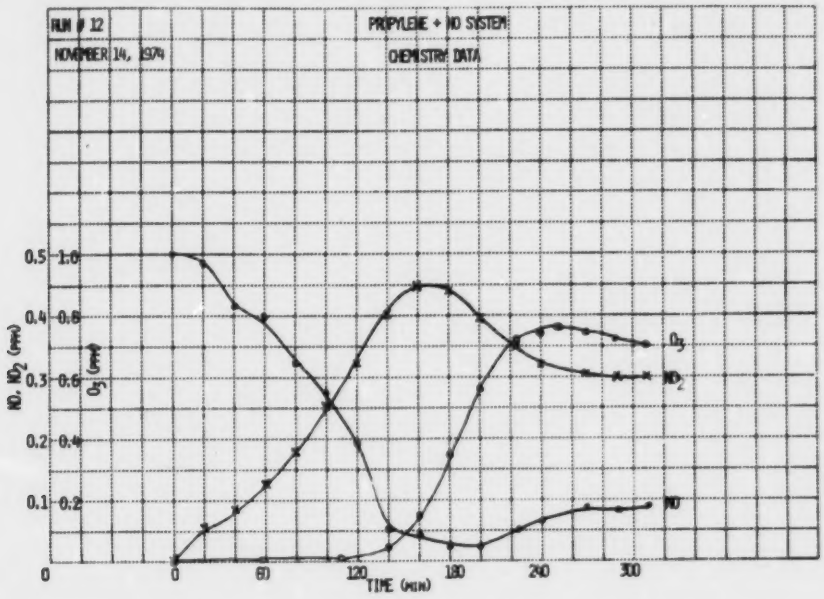

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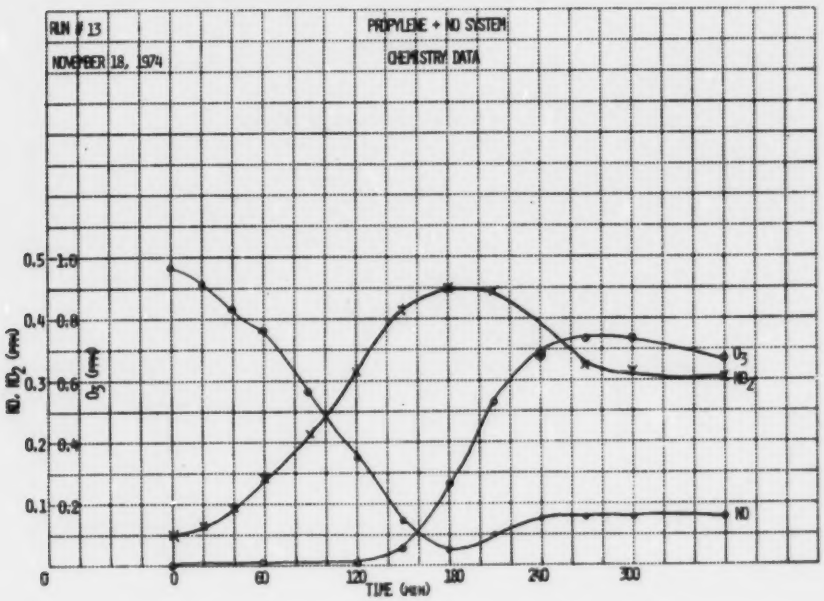

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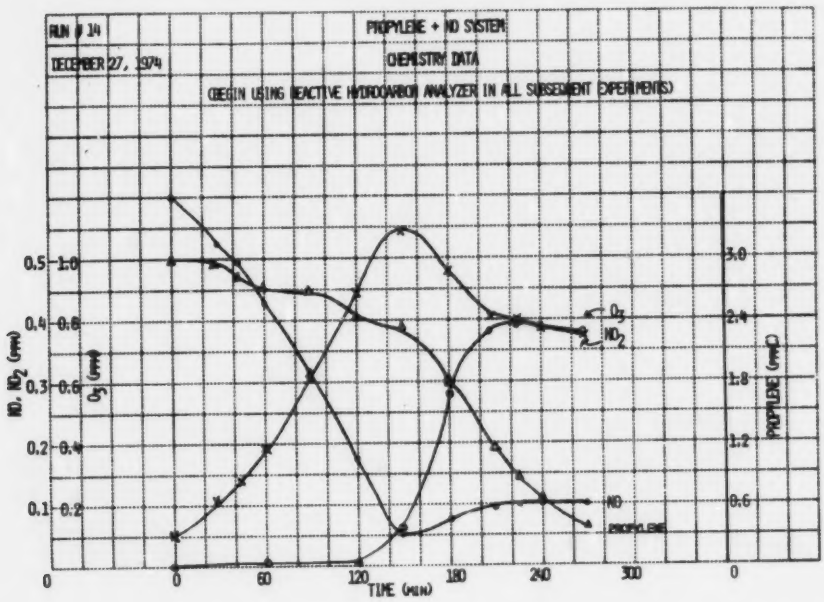

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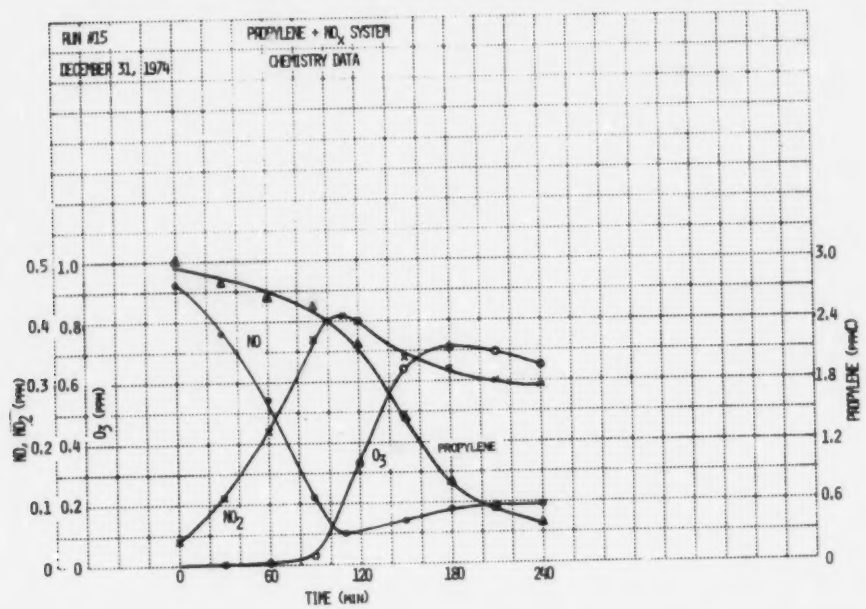

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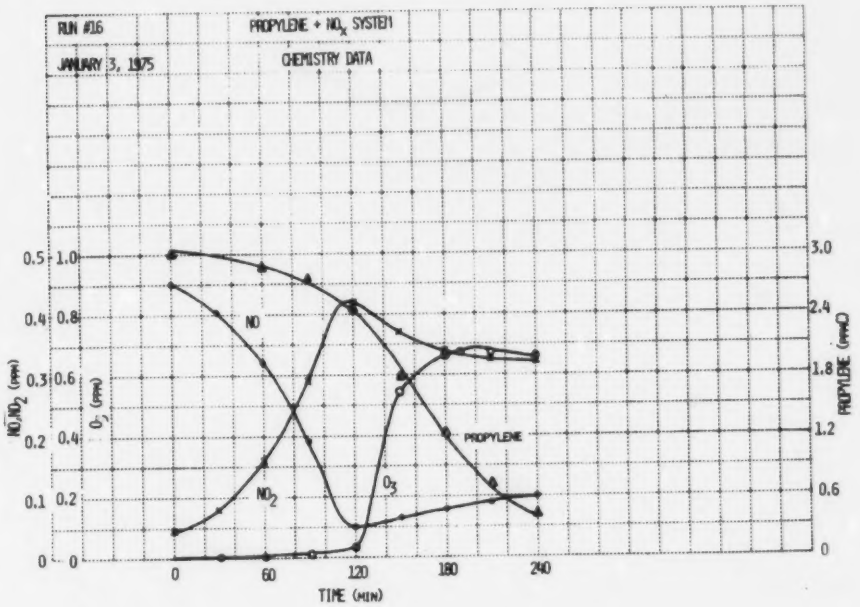

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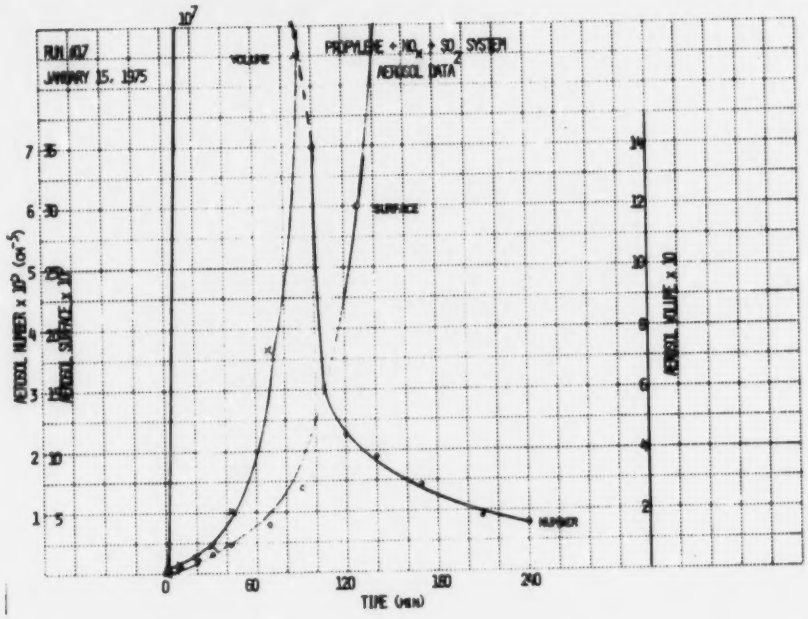

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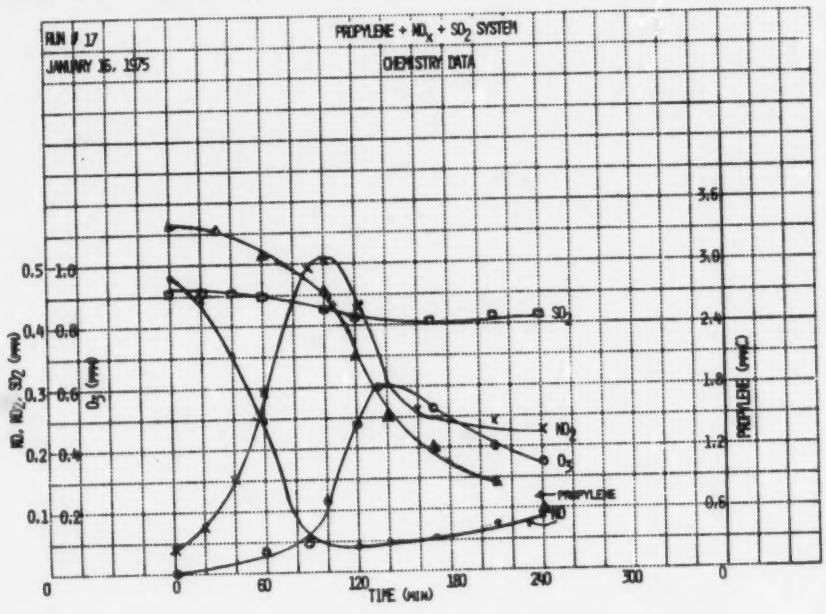

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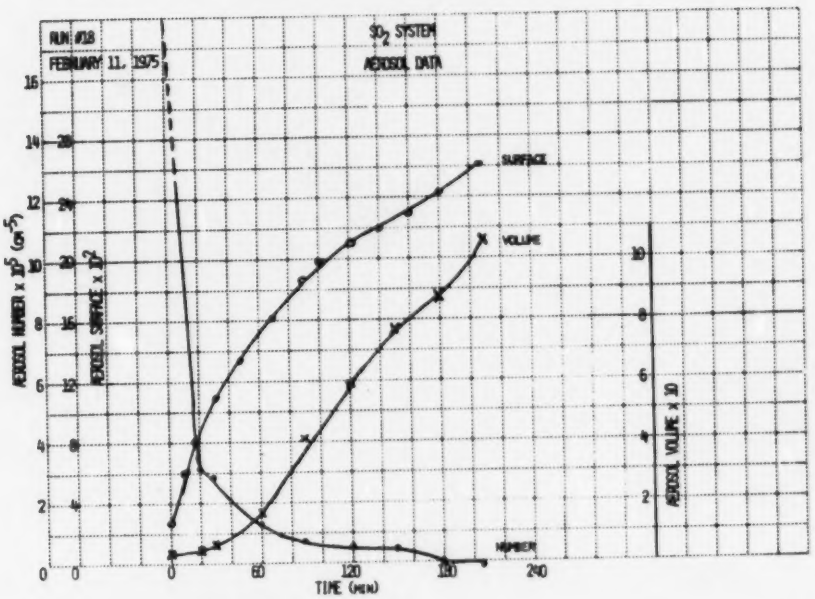

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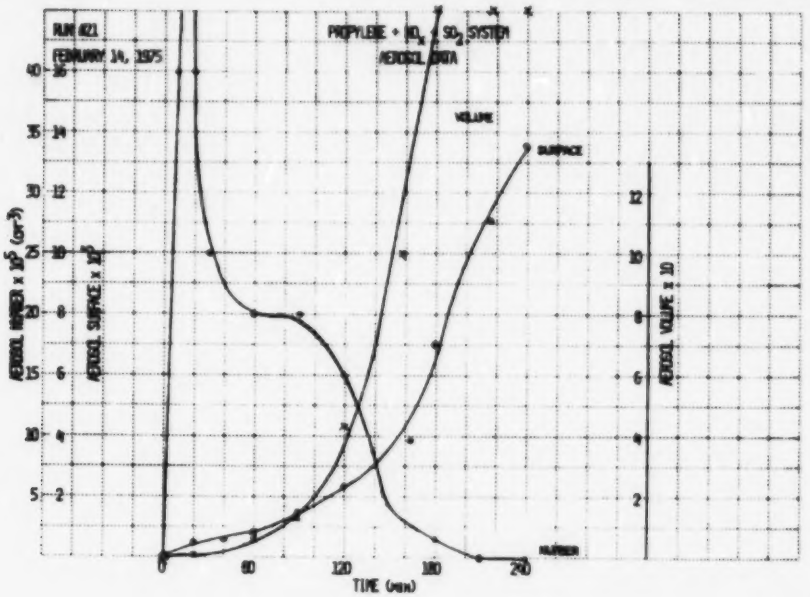
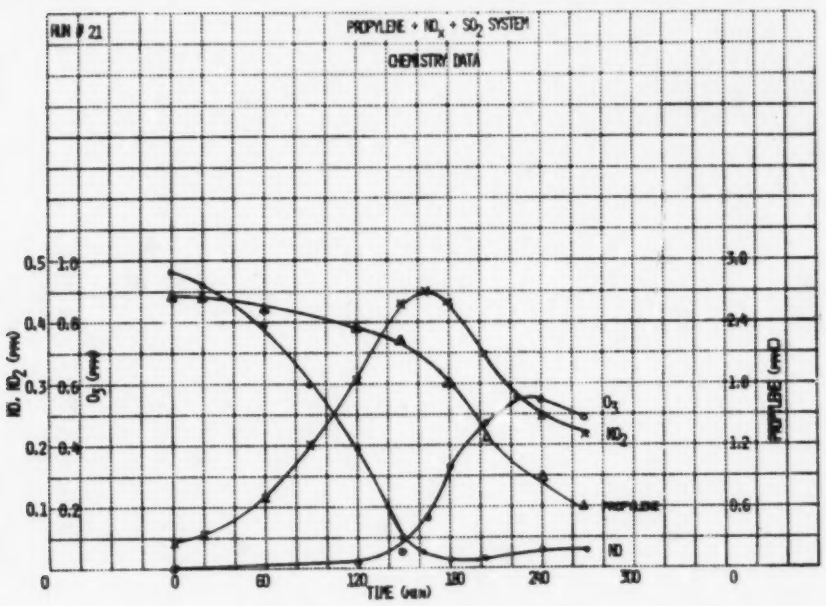
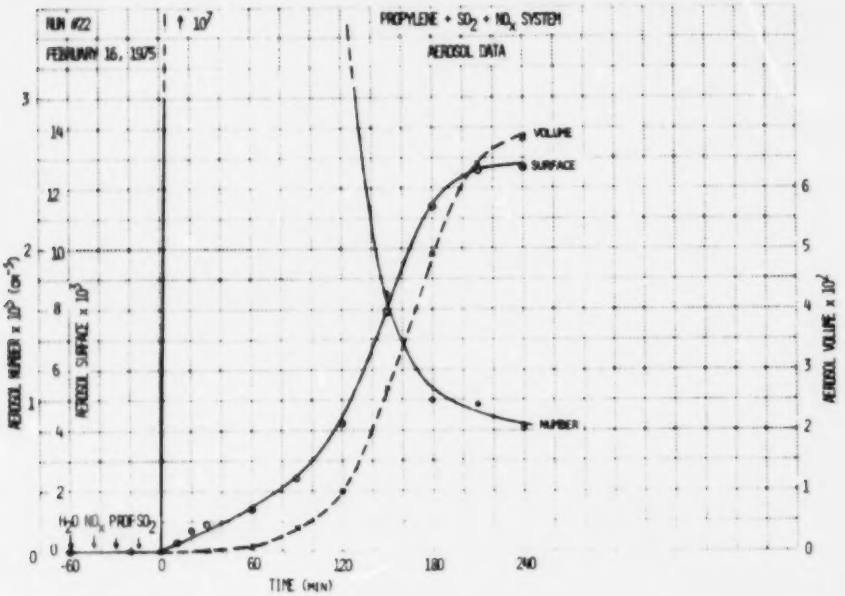


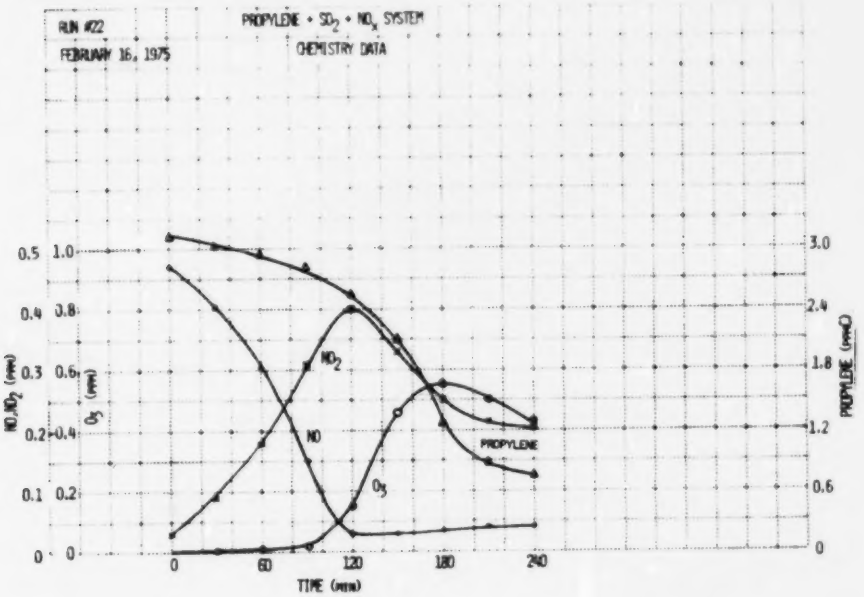
RUN #21 - CHEMISTRY DATA FOR PROPYLENE + NO_x + SO_2 SYSTEM



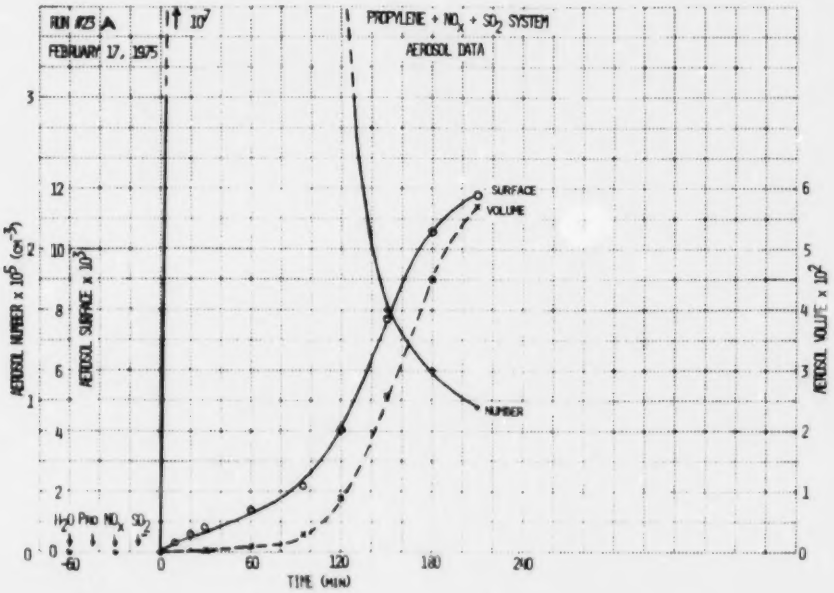
RUN #22 - AEROSOL DATA FOR PROPYLENE + SO_2 + NO_x SYSTEM



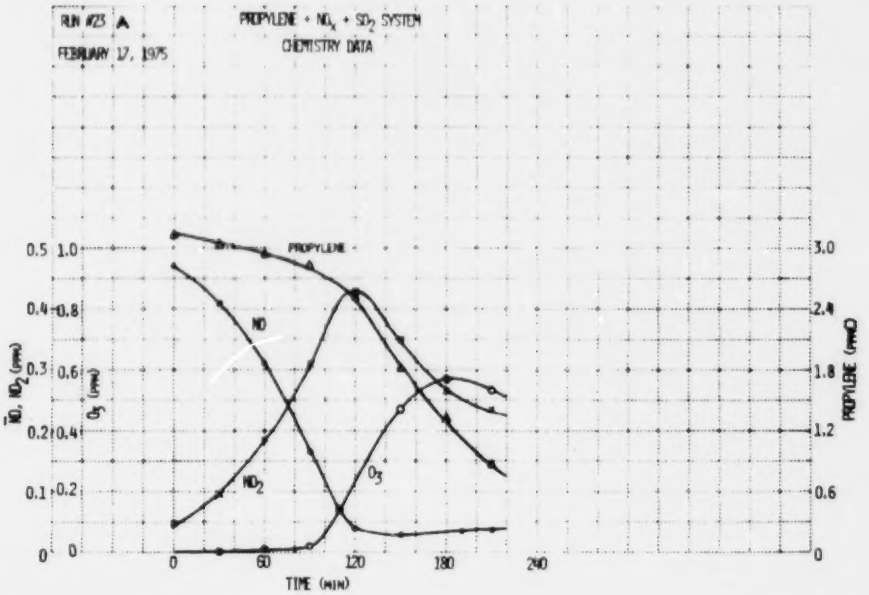
RUN #22 - CHEMISTRY DATA FOR PROPYLENE + SO_2 + NO_x SYSTEM



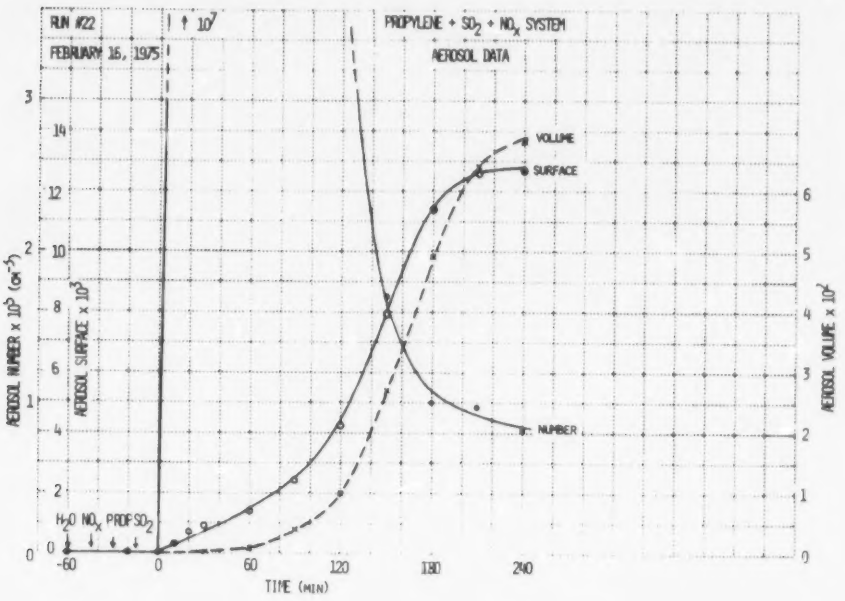
RUN #23A - AEROSOL DATA FOR PROPYLENE + NO_x + SO_2 SYSTEM



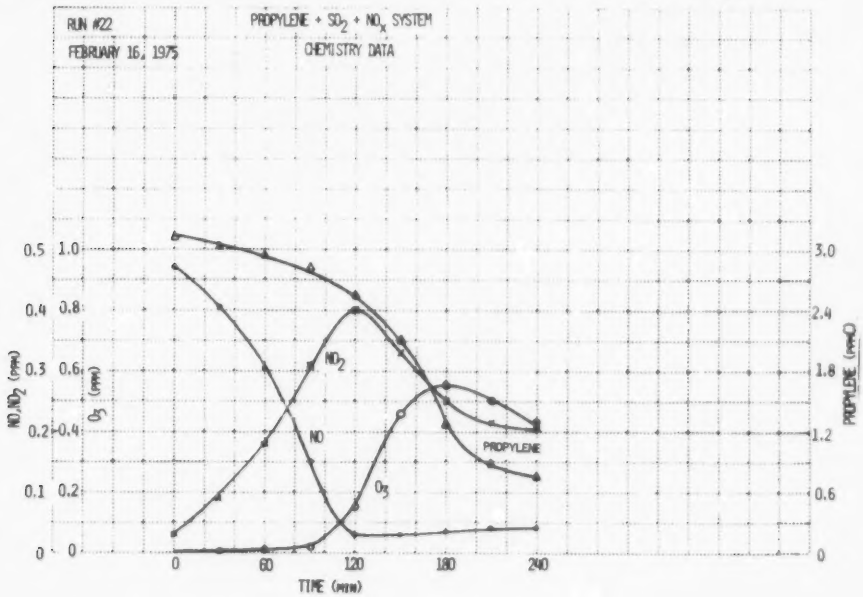
RUN #23A - CHEMISTRY DATA FOR PROPYLENE + NO_x + SO_2 SYSTEM



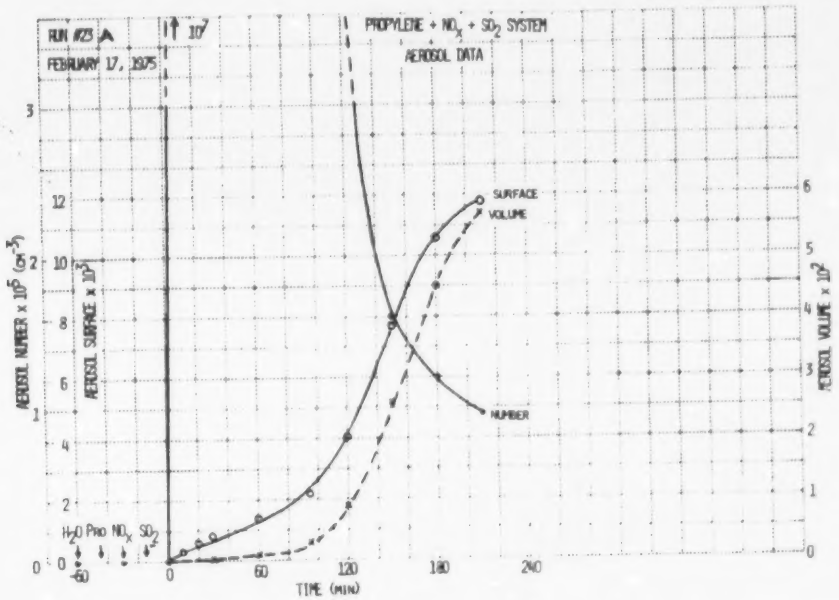
RUN #22 - AEROSOL DATA FOR PROPYLENE + SO_2 + NO_x SYSTEM



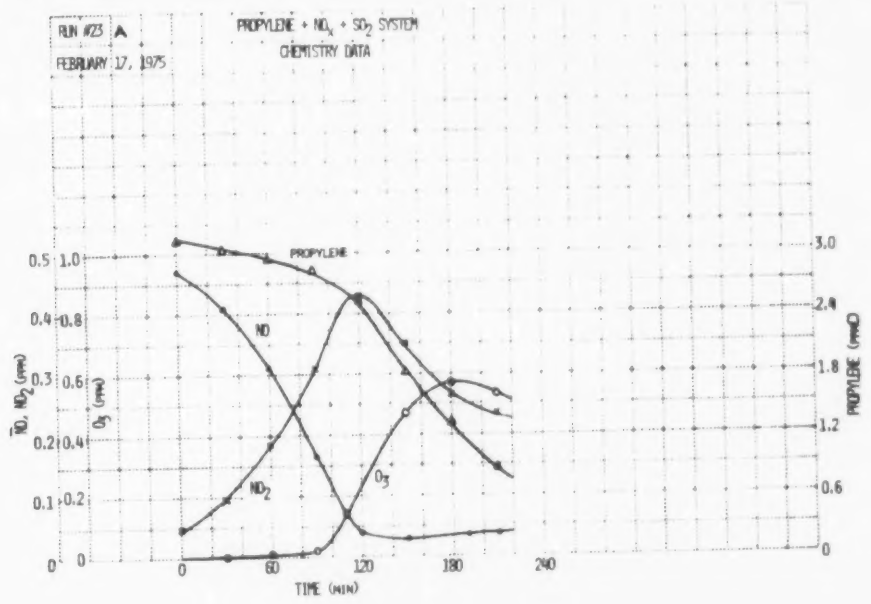
RUN #22 - CHEMISTRY DATA FOR PROPYLENE + SO_2 + NO_x SYSTEM



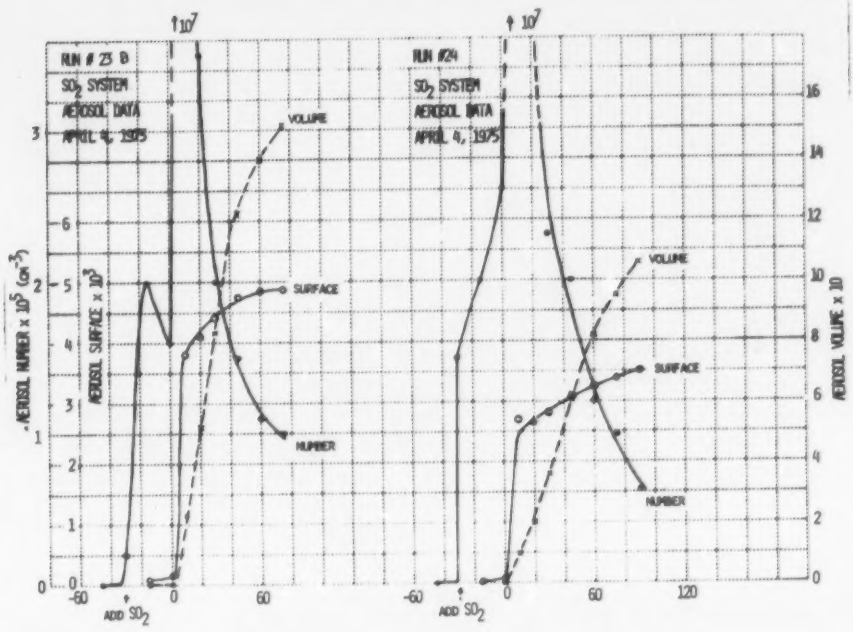
RUN #23A - AEROSOL DATA FOR PROPYLENE + NO_x + SO_2 SYSTEM



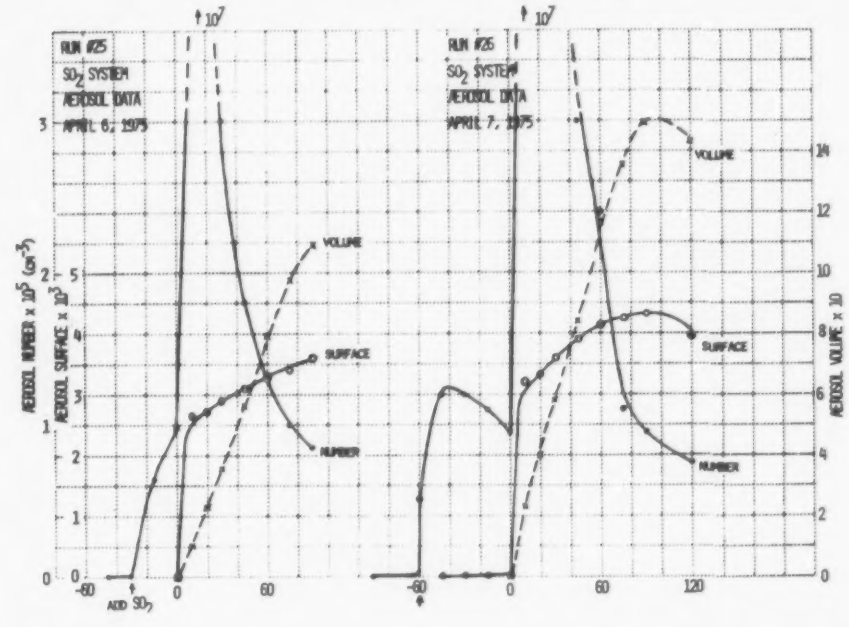
RUN #23A - CHEMISTRY DATA FOR PROPYLENE + NO_x + SO_2 SYSTEM



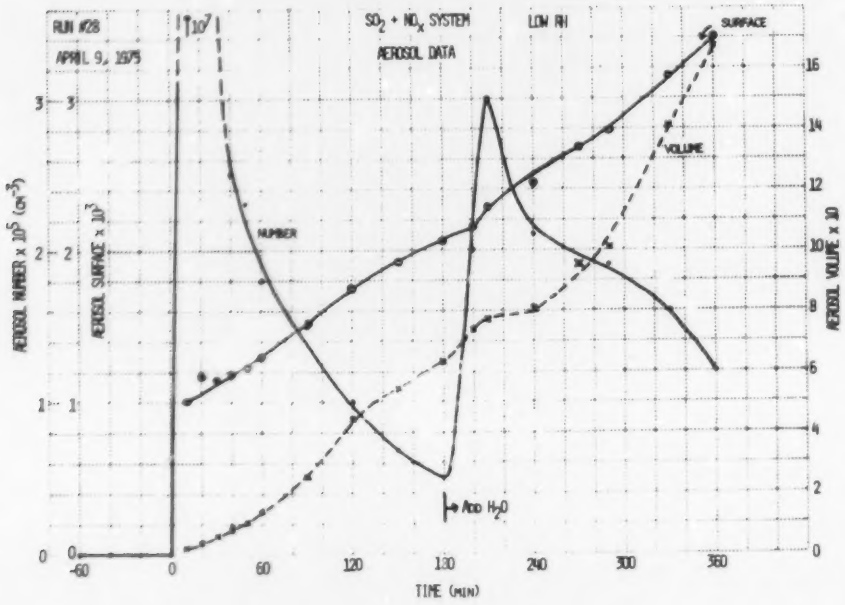
RUN #23B & #24 - AEROSOL DATA FOR SO_2 SYSTEM



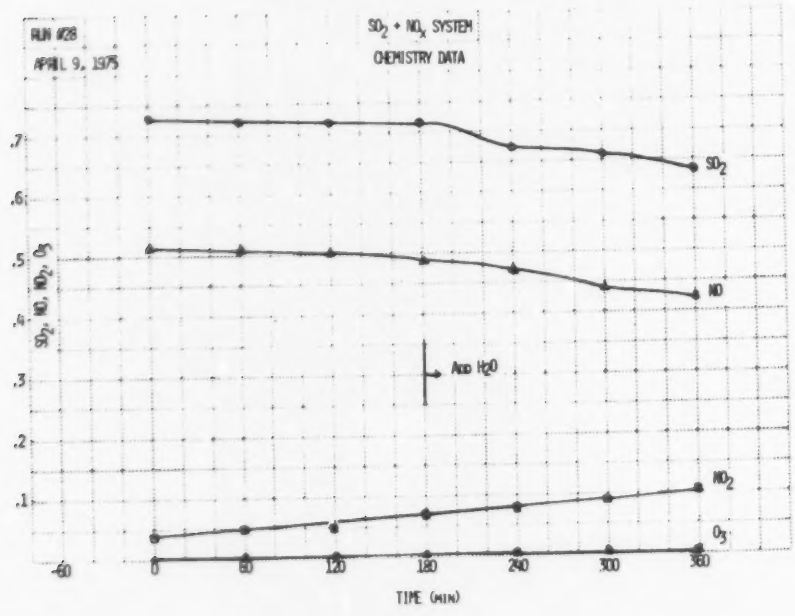
RUN #25 & #26 - AEROSOL DATA FOR SO_2 SYSTEM



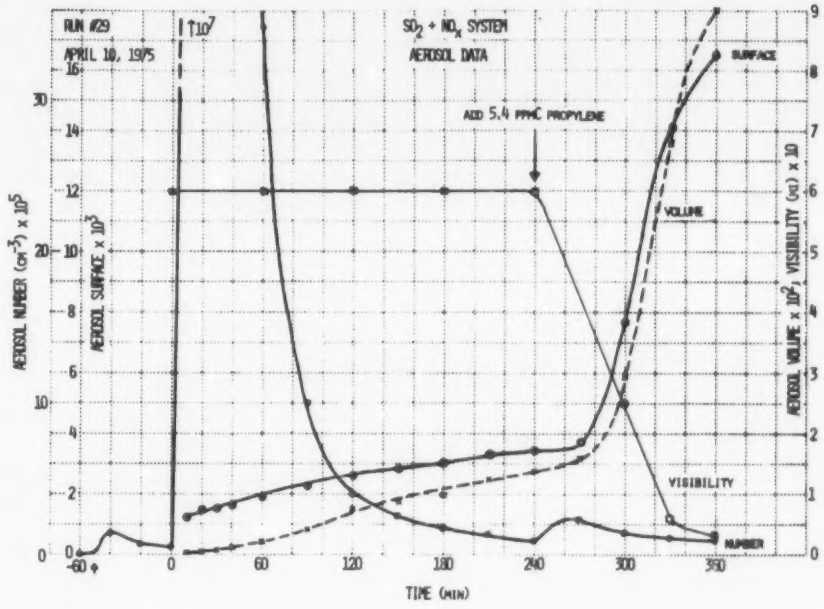
RUN #28 - AEROSOL DATA FOR $SO_2 + NO_x$ SYSTEM



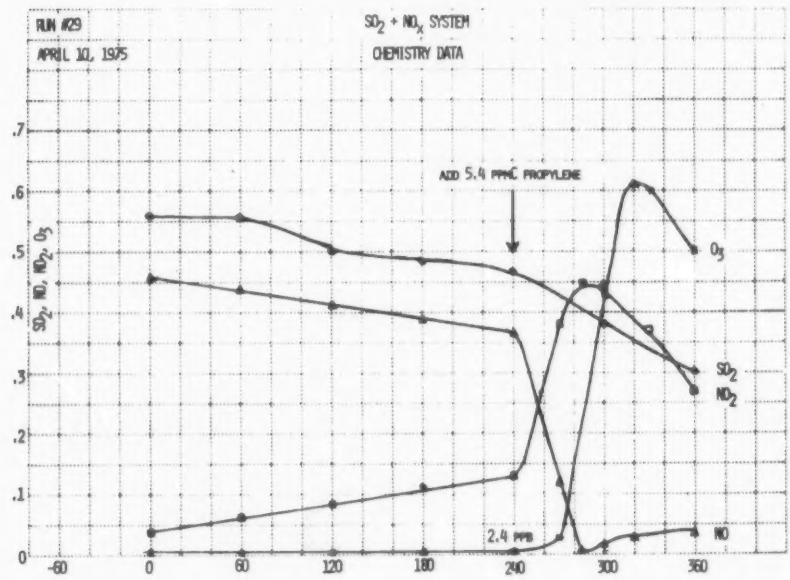
RUN #28 - CHEMISTRY DATA FOR $SO_2 + NO_x$ SYSTEM



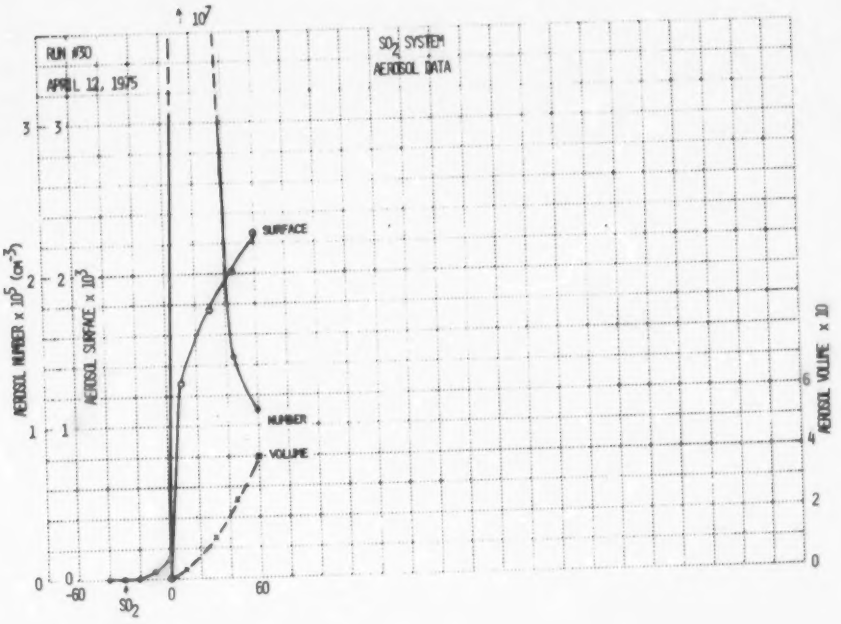
RUN #29 - AEROSOL DATA FOR SO_2 + NO_x SYSTEM



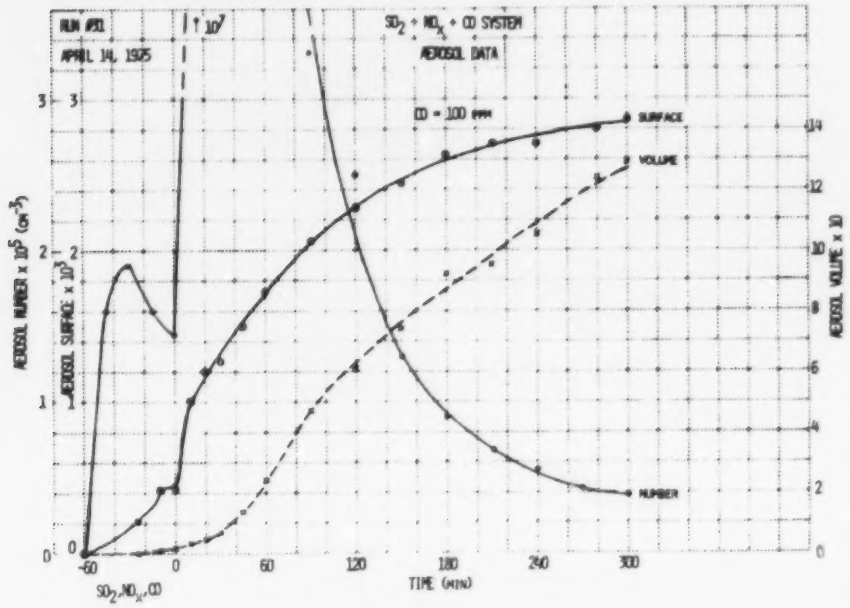
RUN #29 - CHEMISTRY DATA FOR SO_2 + NO_x SYSTEM



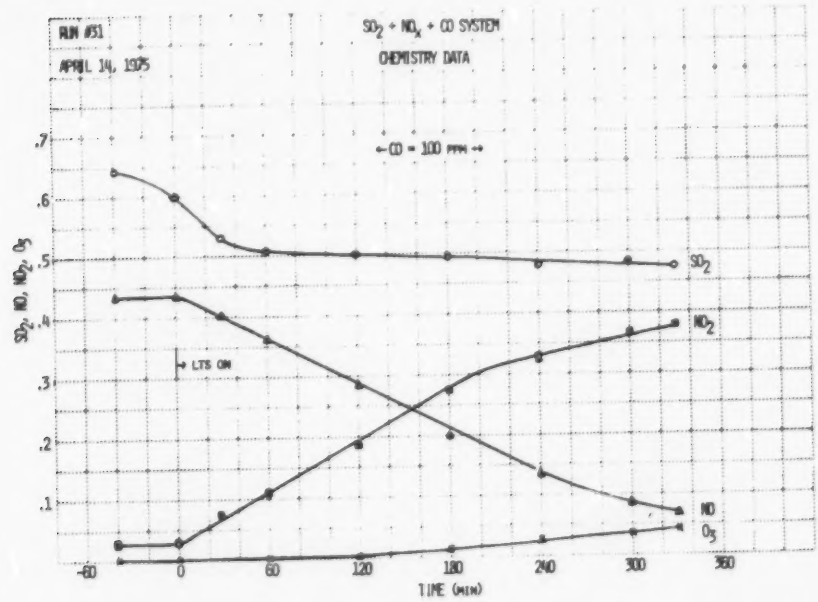
RUN #30 - AEROSOL DATA FOR SO_2 SYSTEM



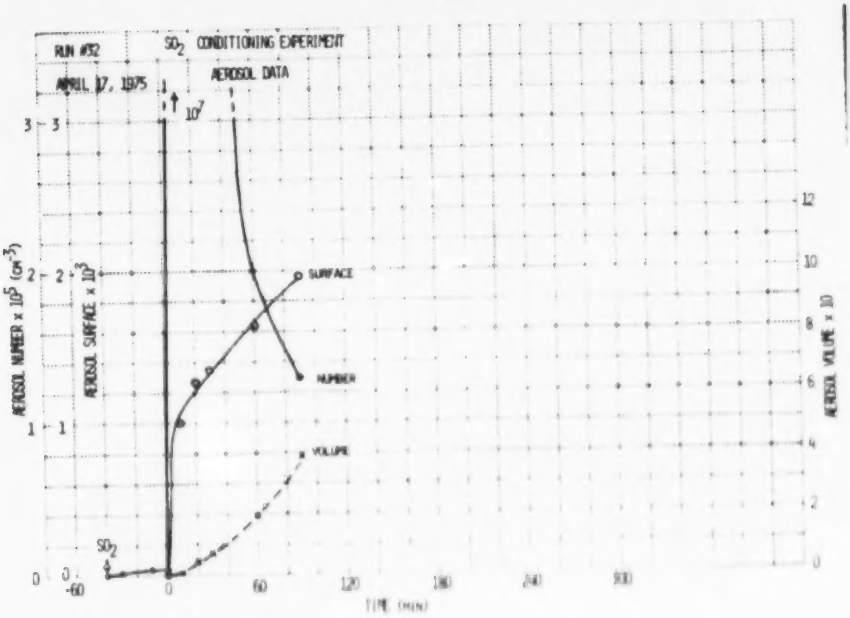
RUN #31 - AEROSOL DATA FOR SO_2 + NO_x + CO SYSTEM



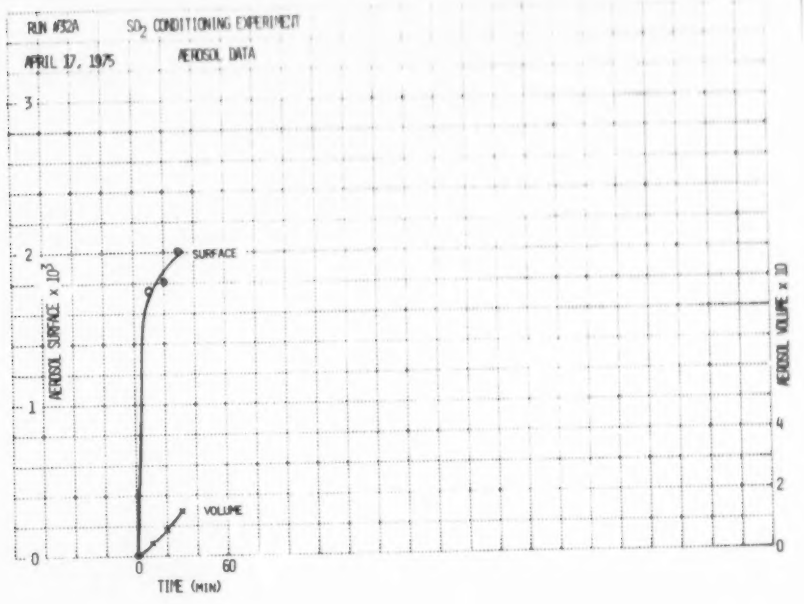
RUN #31 - CHEMISTRY DATA FOR SO_2 + NO_x + CO SYSTEM



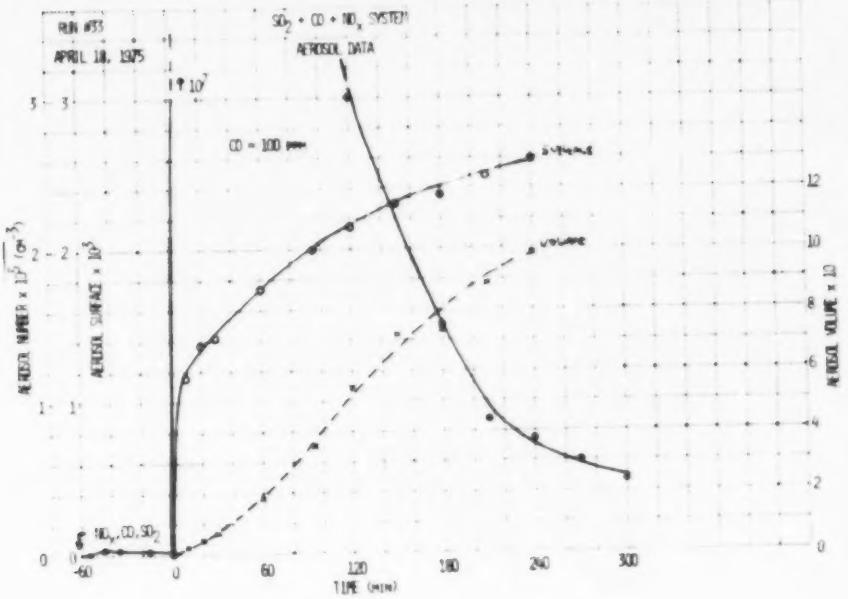
RUN #32 - AEROSOL DATA FOR SO_2 CONDITIONING EXPERIMENT



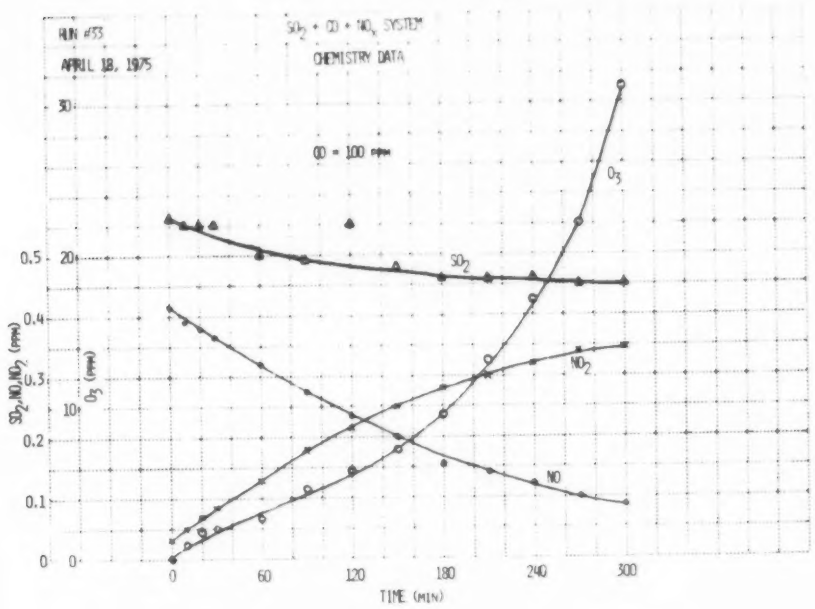
RUN #32A - AEROSOL DATA SO_2 CONDITIONING EXPERIMENT



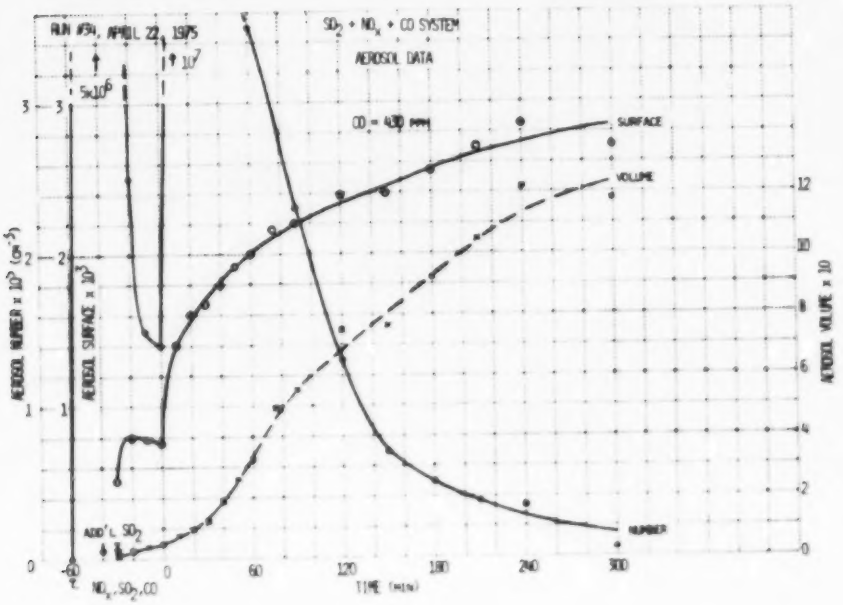
RUN #33 - AEROSOL DATA FOR SO_2 + CO + NO_x SYSTEM



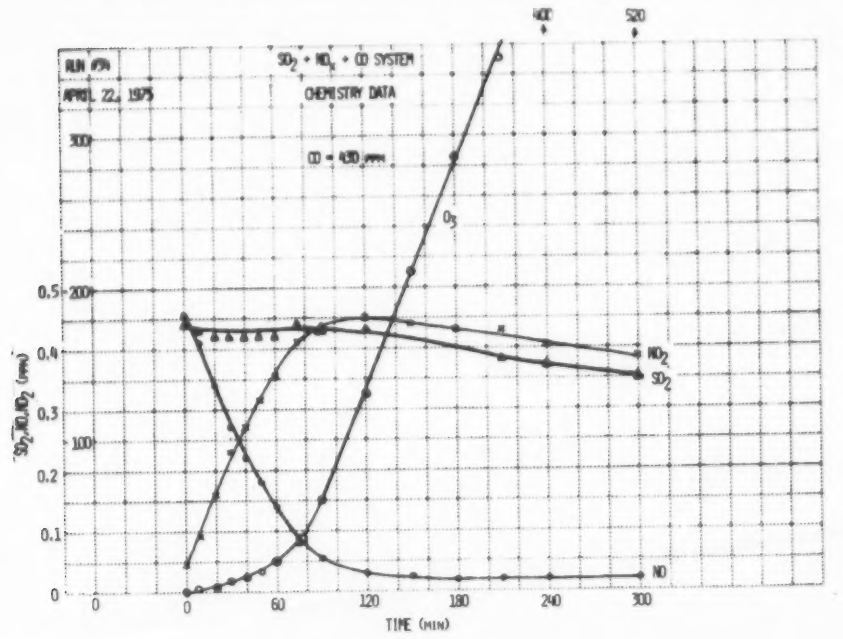
RUN #33 - CHEMISTRY DATA FOR SO_2 + CO + NO_x SYSTEM



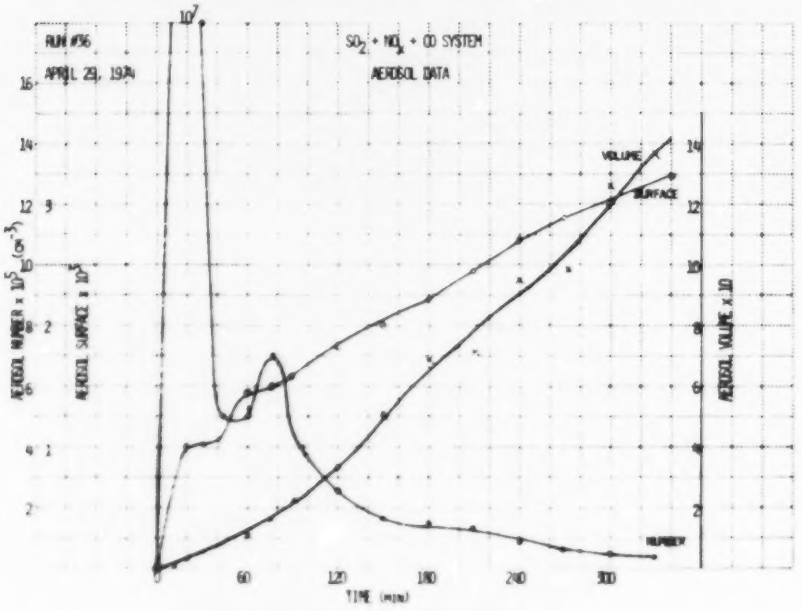
RUN #34 - AEROSOL DATA FOR $SO_2 + NO_x + CO$ SYSTEM



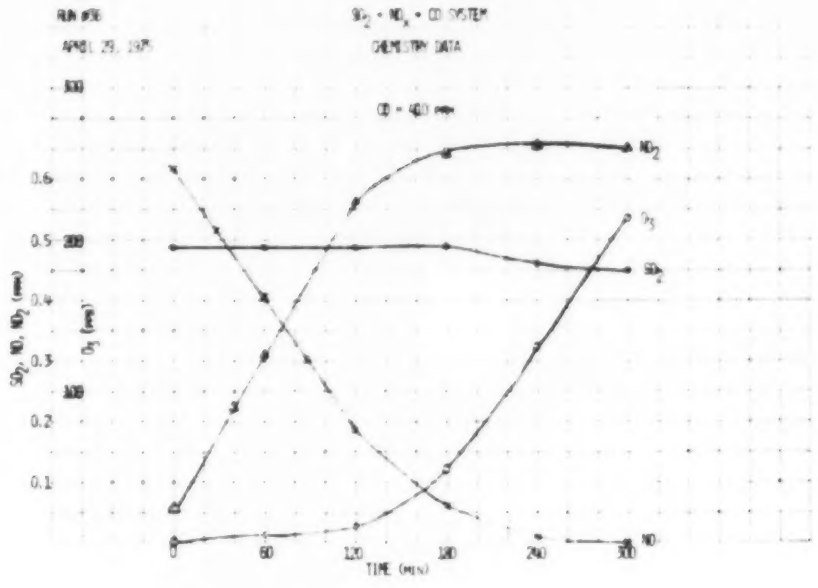
RUN #34 - CHEMISTRY DATA FOR $SO_2 + NO_x + CO$ SYSTEM



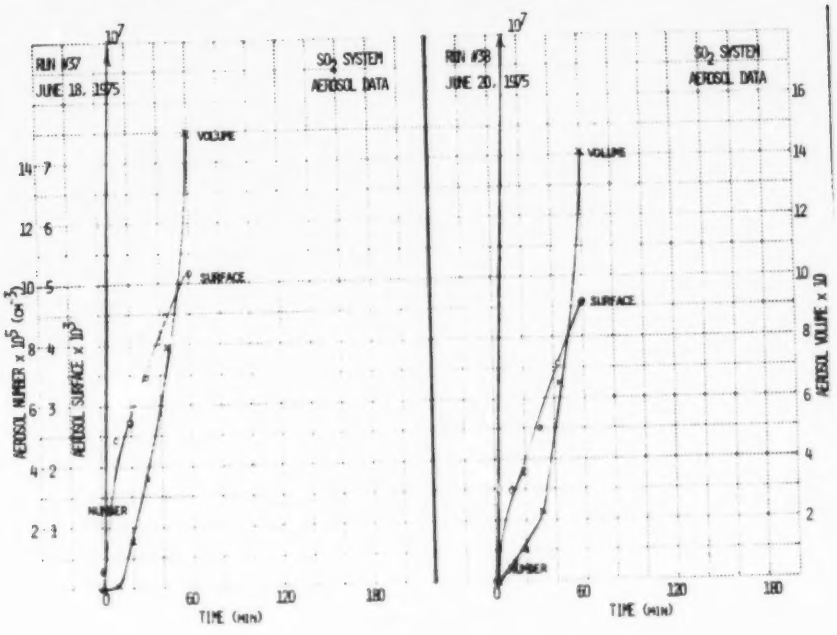
RUN #36 - AEROSOL DATA FOR $SO_2 + NO_x + CO$ SYSTEM



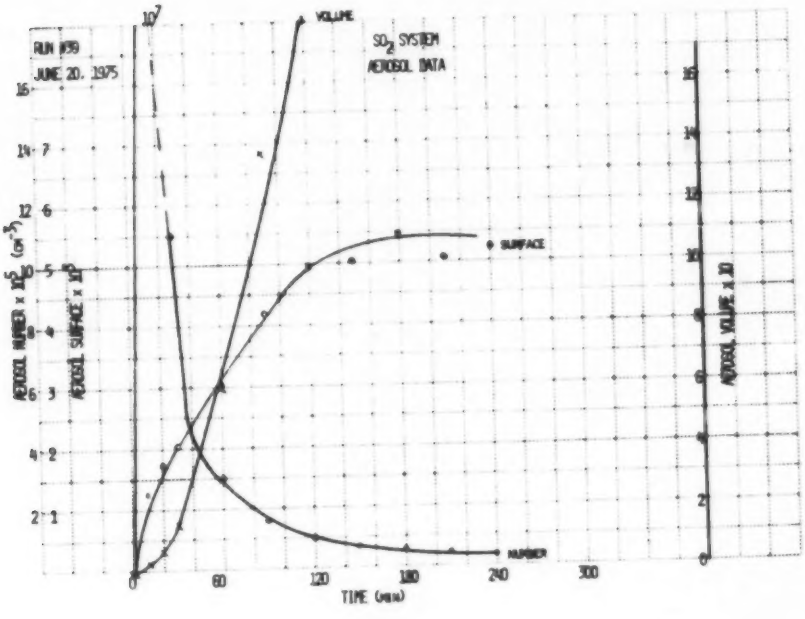
RUN #36 - CHEMISTRY DATA FOR $SO_2 + NO_x + CO$ SYSTEM



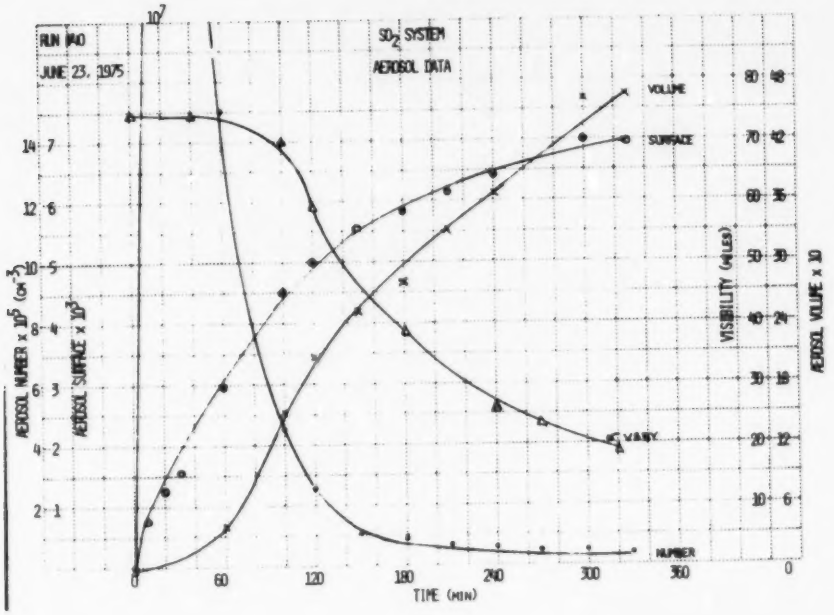
RUNS #37 & #38 - AEROSOL DATA FOR SO_2 SYSTEM



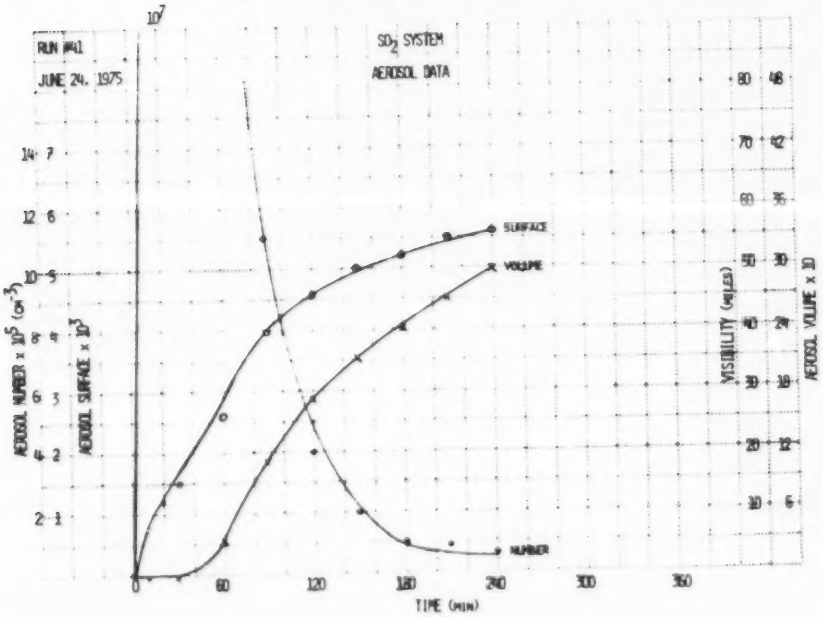
RUN #39 - AEROSOL DATA FOR SO_2 SYSTEM



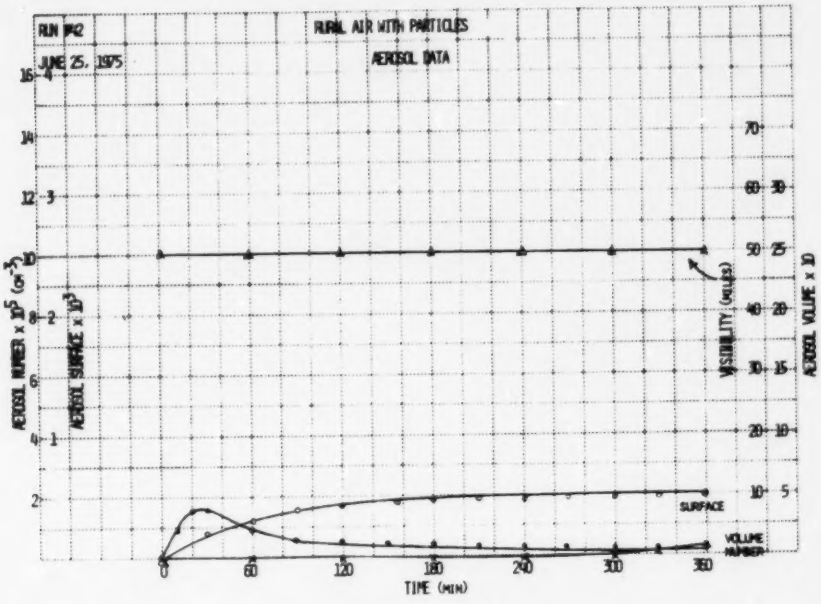
RUN #40 - AEROSOL DATA FOR SO_2 SYSTEM



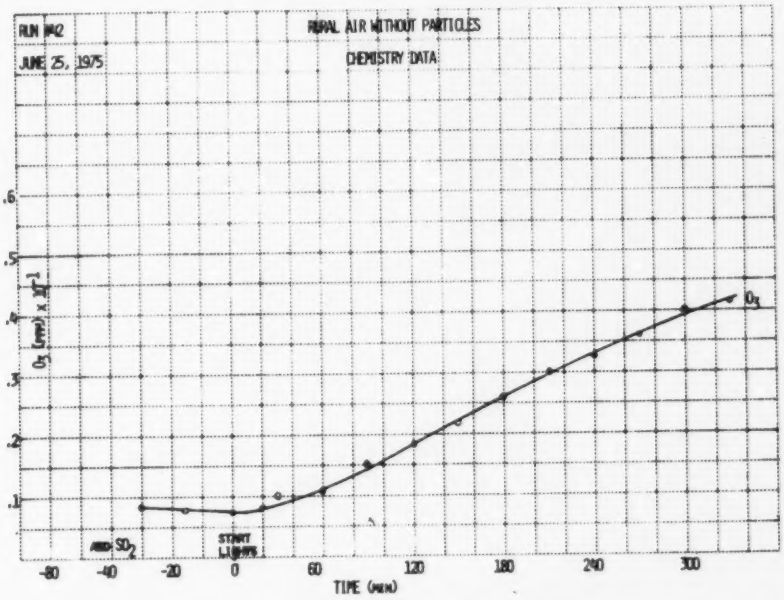
RUN #41 - AEROSOL DATA FOR SO_2 SYSTEM



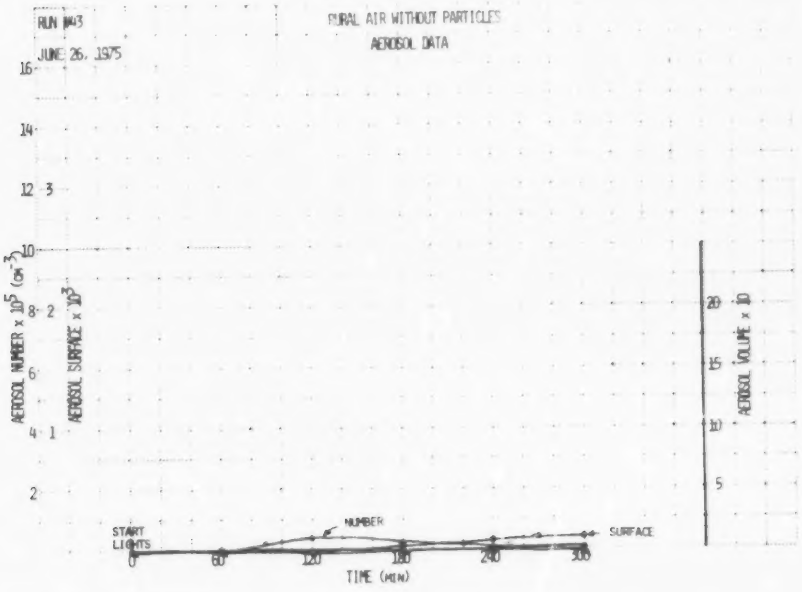
RUN #42 - AEROSOL DATA FOR RURAL AIR WITH PARTICLES SYSTEM



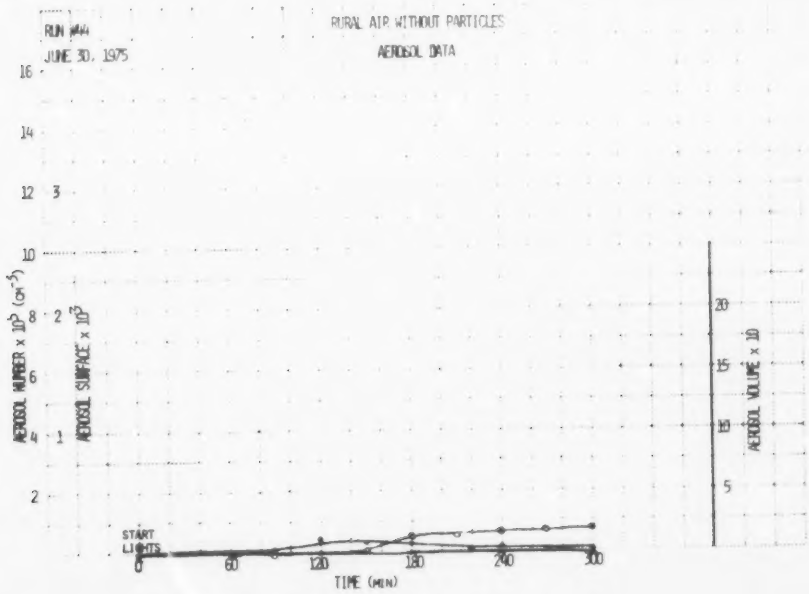
RUN #42 - CHEMISTRY DATA FOR RURAL AIR WITHOUT PARTICLES SYSTEM



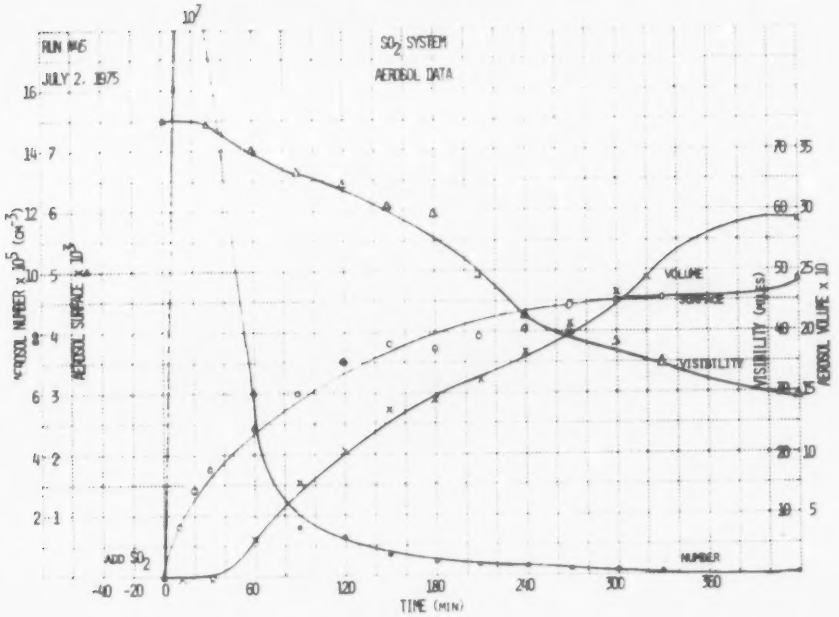
RUN #43 - AEROSOL DATA FOR RURAL AIR WITHOUT PARTICLES SYSTEM



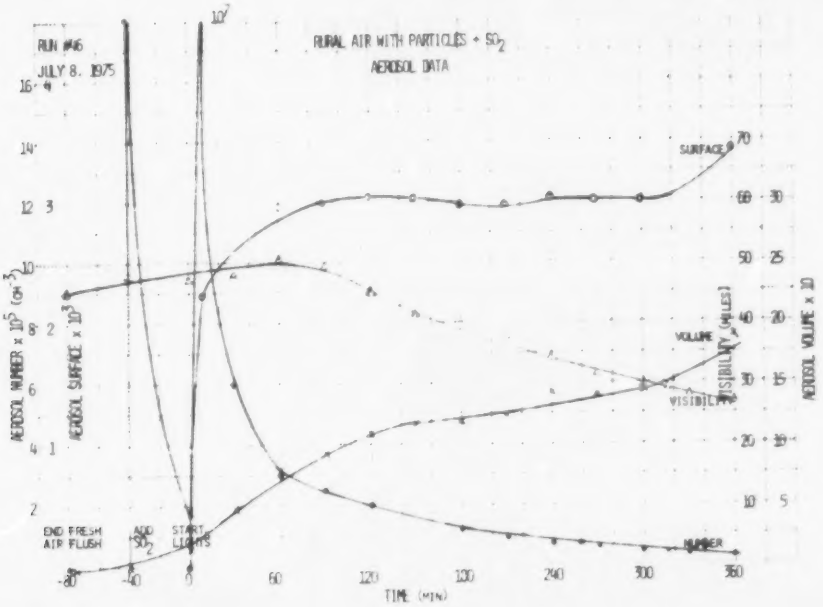
RUN #44 - AEROSOL DATA FOR RURAL AIR WITHOUT PARTICLES SYSTEM



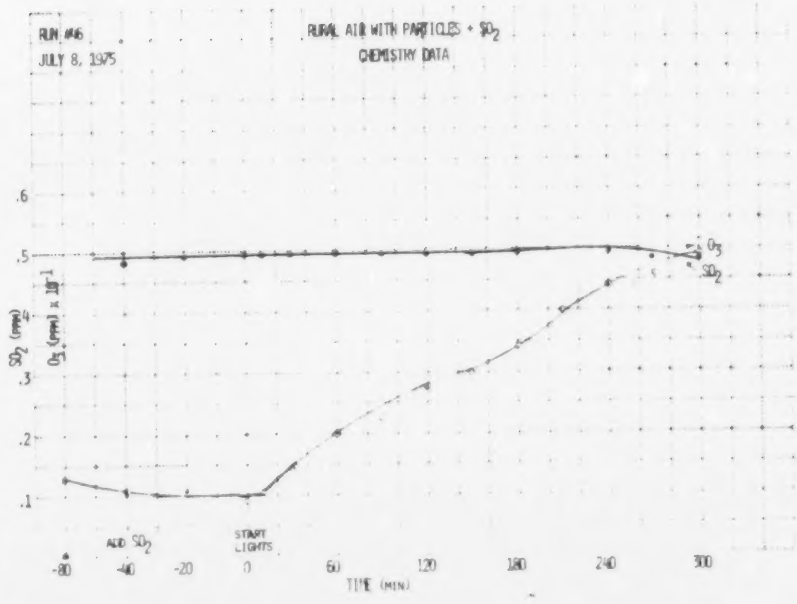
RUN #45 - AEROSOL DATA FOR SO_2 SYSTEM



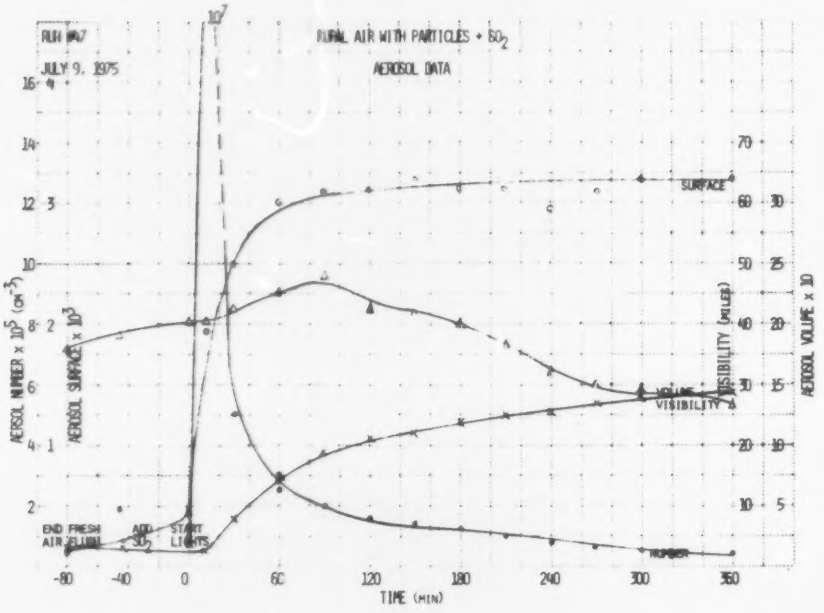
RUN #46 - AEROSOL DATA FOR RURAL AIR WITH PARTICLES + SO_2 SYSTEM



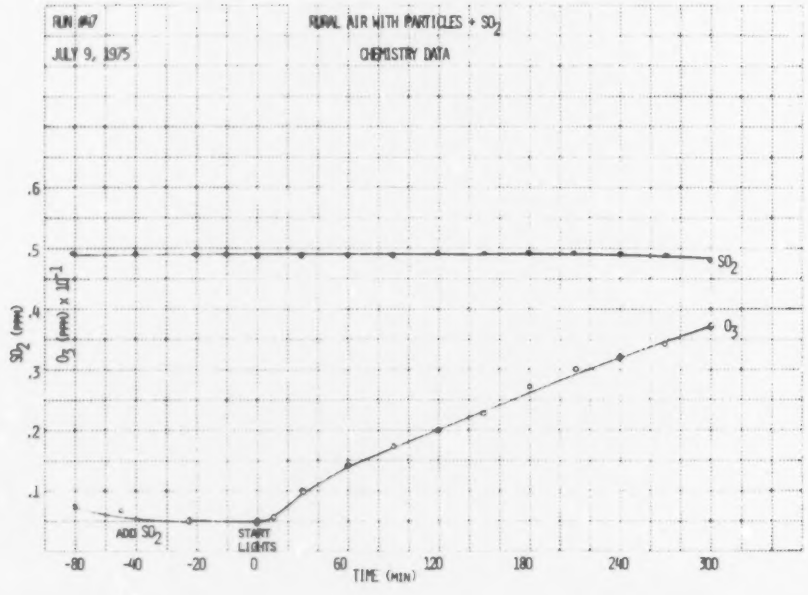
RUN #46 - CHEMISTRY DATA FOR RURAL AIR WITH PARTICLES + SO_2 SYSTEM



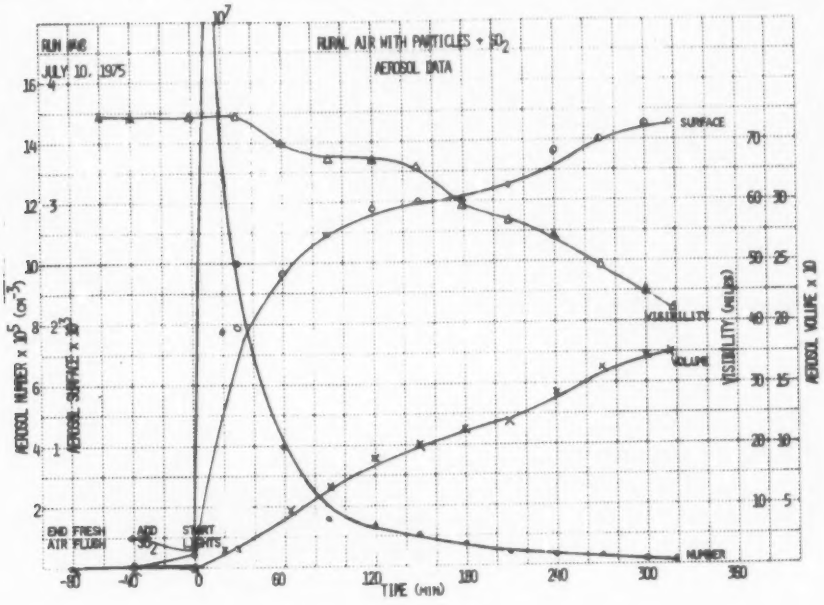
RUN #47 - AEROSOL DATA FOR RURAL AIR WITH PARTICLES + SO_2 SYSTEM



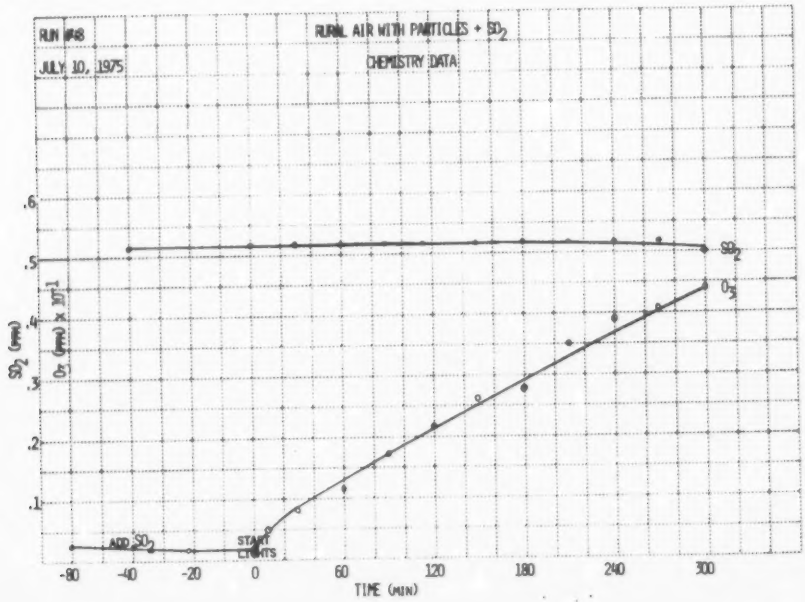
RUN #47 - CHEMISTRY DATA FOR RURAL AIR WITH PARTICLES + SO_2 SYSTEM



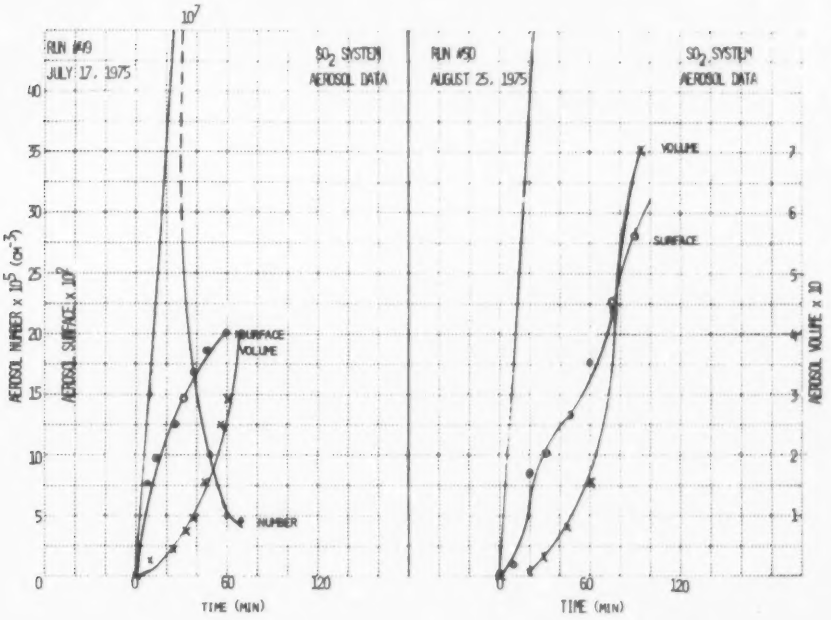
RUN #48 - AEROSOL DATA FOR RURAL WITH PARTICLES + SO_2 SYSTEM



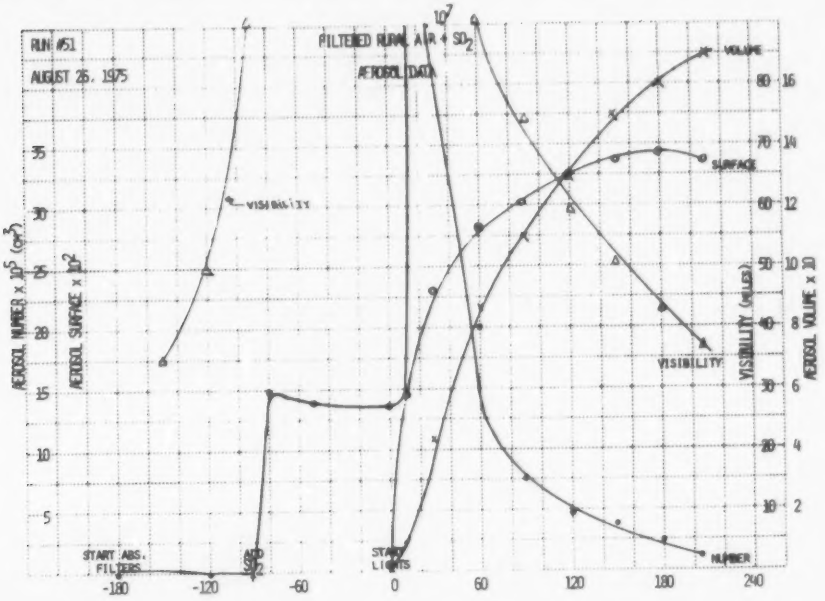
RUN #48 - CHEMISTRY DATA FOR RURAL AIR WITH PARTICLES + SO_2 SYSTEM



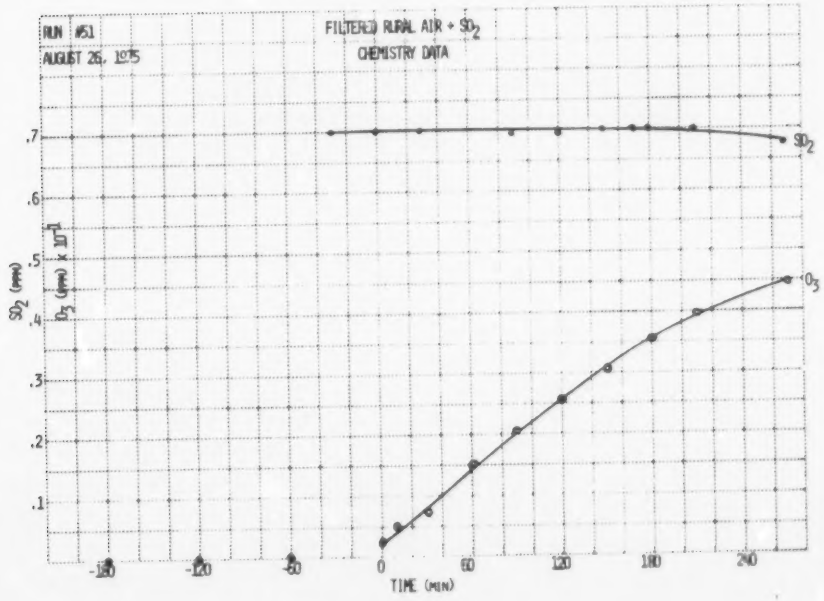
RUNS #49 & #50 - AEROSOL DATA FOR SO_2 SYST



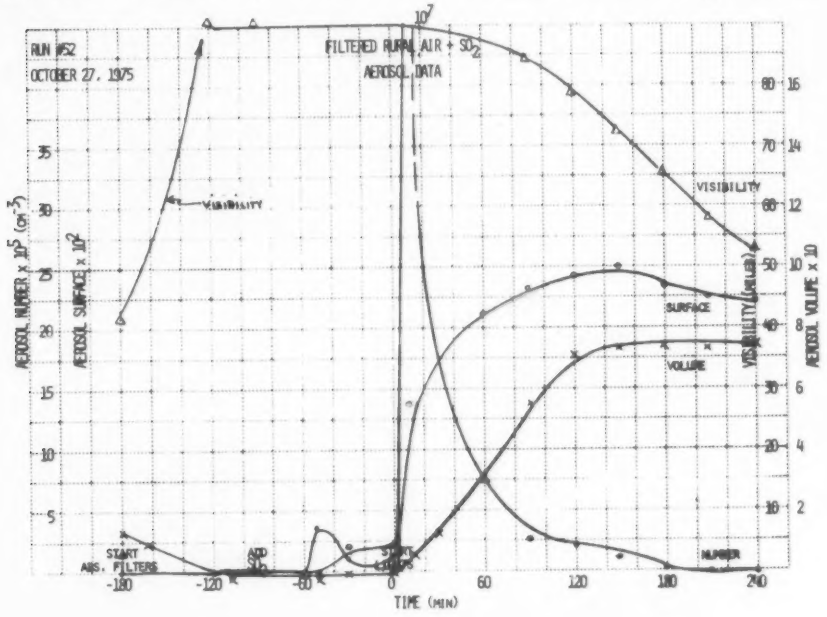
RUN #51 - AEROSOL DATA FOR FILTERED RURAL AIR + SO_2 SYSTEM



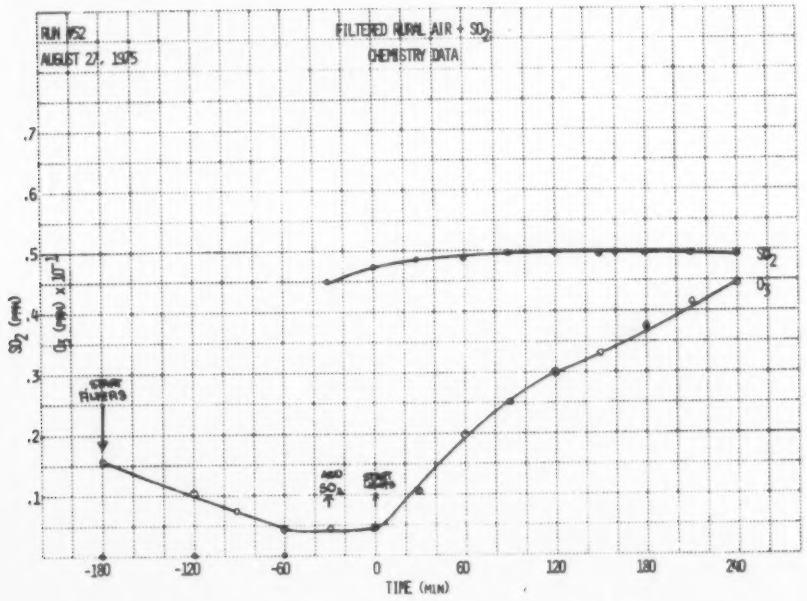
RUN #51 - CHEMISTRY DATA FOR FILTERED RURAL AIR + SO_2 SYSTEM



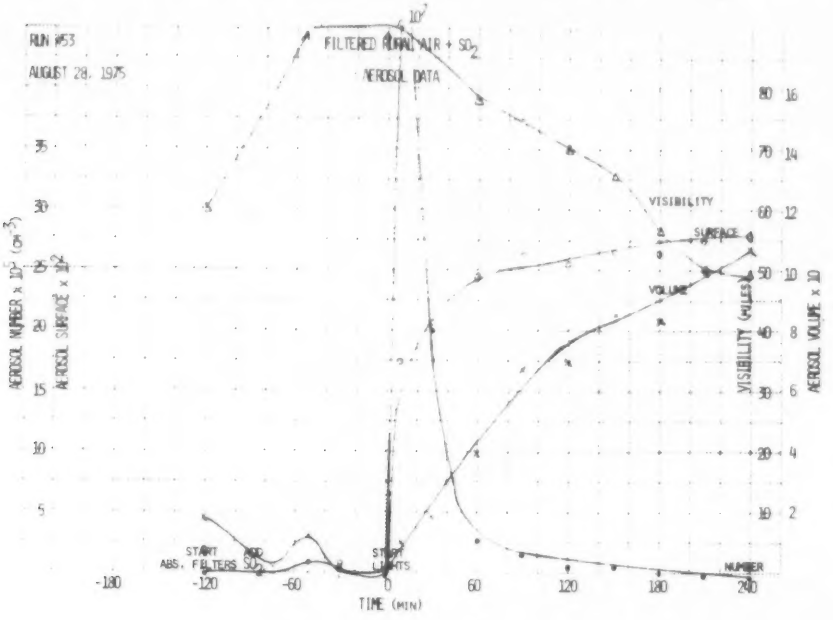
RUN #52 - AEROSOL DATA FOR FILTERED RURAL AIR + SO_2 SYSTEM



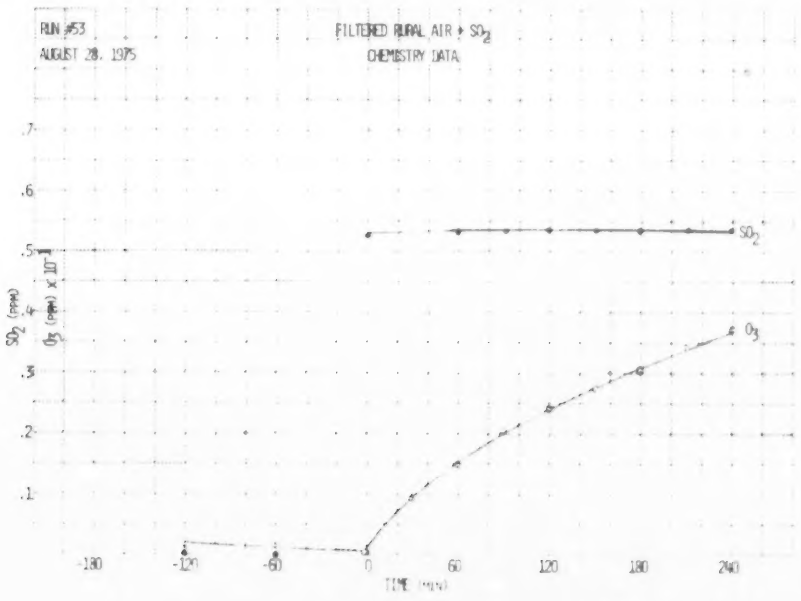
RUN #52 - CHEMISTRY DATA FOR FILTERED RURAL AIR + SO_2 SYSTEM



RUN #53 - AEROSOL DATA FOR FILTERED RURAL AIR + SO_2 SYSTEM



RUN #53 - CHEMISTRY DATA FOR FILTERED RURAL AIR + SO_2 SYSTEM



RUN #54 - AEROSOL DATA FOR SO_2 SYSTEM